Fall 2023 Solid State Ionics

Homework 2

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Problem 1: The exact solution of the potential profile in Gouy-Chapman case

In Lecture 7, we have derived the potential profile in the Gouy-Chapman case with the assumption of a low ϕ_0, so that we can linearize the equation. In this problem, we are going to relax this assumption and find the exact solution of the potential profile of the Gouy-Chapman case.

1. The same as we have discussed in Lecture 7, consider two mobile defects with opposite charge ze and -ze, a bulk concentration of c_∞ and a positive core charge Q_{core}. Express **1)** the concentrations of these two mobile defects ($c_+(x)$ and $c_-(x)$) **2)** charge density $\rho(x)$ **3)** Poisson's equation **as a function of position** x and **electrostatic potential** ϕ.

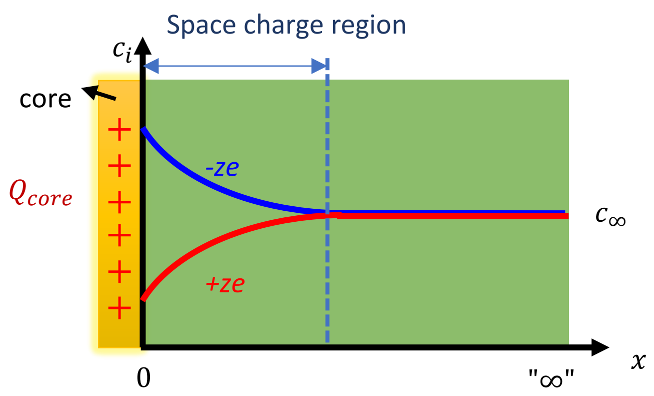

Figure 1 Space charge layer: Gouy-Chapman case

2. Solve the Poisson's equation analytically by taking the steps below:
   a) Notice $\frac{d^2\phi}{dx^2} = \frac{1}{2}\frac{d}{d\phi}(\frac{d\phi}{dx})^2$, try to find the solution for $(\frac{d\phi}{dx})^2$
   b) Consider the position far away from the space charge core ($x = \infty$), we should have: $\phi(\infty) = 0$ and $\left.\frac{d\phi}{dx}\right|_{x=\infty} = 0$. Find the solution for $\frac{d\phi}{dx}$ based on this boundary condition. **Think carefully which square root you should choose** when you go from $(\frac{d\phi}{dx})^2$ to $\frac{d\phi}{dx}$. (***Note:*** you will need the expression for $\frac{d\phi}{dx}$ in problem 2)
   c) Try to solve the integral and find the solution for $\phi(x)$. You can simplify the solution by denoting the potential at $x = 0$ as ϕ_0 and defining the Debye length (also write down the expression for the Debye length). **Hint**: you might find this integral useful: $\int \frac{1}{\sinh(x)} = \ln\left(\tanh\left(\frac{x}{2}\right)\right) + C$.

3. Use your favorite scientific graphing software/code (*e.g.*, Originlab, Python Matplotlib, Matlab) to plot the following cases:
   a) z = 1, c_∞ = 1 mM, ε_r= 5, plot normalized electrostatic potential profile $\phi(x)/\phi_0$ for **1)** ϕ_0 = 10 mV, **2)** ϕ_0 = 100 mV, **3)** ϕ_0 = 1000 mV in the same plot.
   b) z = 1, ε_r= 5, ϕ_0 = 100 mV, plot normalized electrostatic potential profile $\phi(x)/\phi_0$ with x/λ_D as *x*-axis for **1)** c_∞ = 10^{20} cm^{-3}, **2)** c_∞ = 10^{21} cm^{-3}, 3**)** c_∞ = 10^{22} cm^{-3}

Problem 2: The capacitance of a space charge layer

In this question, we are going to reach the expression for the capacitance of a space charge layer. Again, we consider the Gouy-Chapman case, similar to that in question 1.

1. According to Gauss law in 1D, the core charge will have the expression below:

$$Q_{core} = \varepsilon_0 \varepsilon_r \frac{d\phi}{dx}\bigg|_{x=0}$$

   where Q_{core} is the charge density at the core. Write down the expression for Q_{core} by using the conclusion you reached in Problem 1.2b. (***Note:*** $\phi(x=0) = \phi_0$)

2. Then the capacitance of the space charge layer is define as:

$$C_D = \frac{dQ_{core}}{d\phi_0}$$

   from the equation above, try to come up with the expression for C_D.

3. Use your favorite scientific graphing software/code (*e.g.*, Originlab, Python Matplotlib, Matlab) to plot the following cases:
   z = 1, ε_r= 5, plot C_D as a function of ϕ_0 (within the range of $-150\, mV < \phi_0 < 150\, mV$) 1) c_∞ = 10^{20} cm^{-3}, 2) c_∞ = 10^{21} cm^{-3}, 3) c_∞ = 10^{22} cm^{-3}

4. Explain why the C_D calculated above is **unphysical** under very positive or very negative ϕ_0. To correct that, we introduce so-called Stern correction, which introduce a "compact layer" between the core and the space charge layer with a finite length ***d***. Then the total capacitance is the serial summation of both the capacitance from the Stern layer (denoted as C_H and that from the space charge layer C_D. Shown as below:

Figure 2 Capacitance with a Stern layer

   C_H has a simple expression as:

$$C_H = \frac{\varepsilon_0 \varepsilon_r}{d}$$

   Try to reach the expression for the total capacitance, denoted as C_{GCS} (subscript for "Gouy-Chapman-Stern") and explain why this resolves the issue at very positive or very negative ϕ_0.

Bonus Problem: Solution to the diffusion equation with two ion-blocking electrodes

In this problem, we are going to solve the diffusion equation in Yokota *et al.*, *J. Phys. Soc. Jpn.*, 1961, step by step. The diffusion equation we need to solve is the following:

$$\frac{\partial c(x,t)}{\partial t} = D^\delta \frac{\partial^2 c(x,t)}{\partial x^2}$$

With the boundary conditions written as:

$$\left.\frac{\partial c(x,\ t)}{\partial x}\right|_{x=0,\ L} = \frac{Fj}{\sigma_e}\frac{c_0}{RT}$$

And initial condition as:

$$c(x,\ 0) = c_0$$

Solve the diffusion equation by taking the steps below:

1. The boundary conditions above are called "non-homogenous" and difficult to handle. It is much easier to handle if the boundary condition is "homogenous", *i.e.*, the derivative equals to zero. Therefore, we use a mathematic trick by rewriting $c(x,\ t)$ as:

   $$c(x,\ t) = u(x,\ t) + v(x)$$

   Which satisfies:

   $$\left.\frac{\partial u(x,\ t)}{\partial x}\right|_{x=0,\ L} = 0$$

   While both $u(x,\ t)$ and $v(x)$ should satisfy the diffusion equation itself. Show that if we choose $v(x) = Ax$, then $v(x)$ satisfy the diffusion equation, *i.e.*,

   $$\frac{\partial v}{\partial t} = D^{\delta}\frac{\partial^2 v}{\partial x^2}$$

   and solve for A by using the boundary conditions (*i.e.*, $u(x,\ t) + v(x)$ should satisfy the boundary condition).

2. Then we solve for $u(x,\ t)$. It is much easier to solve if we can express $u(x,\ t)$ as:

   $$u(x,\ t) = X(x)T(t)$$

   While $X(x)$ and $T(t)$ are functions of x or t only. Then we can rewrite the diffusion equation as:

   $$\frac{1}{D^{\delta}}\frac{T'}{T} = \frac{X''}{X} = -\omega$$

   Explain why ω must be a constant. Then solve for $T(t)$. Since $T(t)$ cannot be infinitely large when $t \to \infty$, explain why ω must be positive.

3. Then we solve for $X(x)$. Since ω must be positive, we can express ω as $\omega = \lambda^2$. Show that the following function can satisfy the equation above:

   $$X(x) = C\sin\lambda x + D\cos\lambda x$$

   Consider the boundary condition for $u(x,\ t)$, show that we must have:

   $$C = 0 \text{ and } \lambda L = n\pi, n = 0, 1, 2, \ldots$$

4. With the results obtained above, we now know that a number of different $X(x)$ with different n ($n = 0, 1, 2, \ldots$) can all satisfy the equation. We can denote them as $X_n(x)$, then we have:

   $$u(x,\ t) = \sum_{n=0}^{\infty} X_n(x)T_n(t) = \sum_{n=0}^{\infty} D_n \cos\lambda_n x\, T_n(t)$$

   and we know that $\lambda_n L = n\pi$. We need to find out the values for $D_n$by using the initial condition. In order to do that, we have:

   $$u(x,\ 0) = \sum_{n=0}^{\infty} D_n \cos\lambda_n x = c(x,\ 0) - v(x)$$

   To solve the equation above, we multiply both side by $\cos\lambda_m x$, then integrate from $x =$

0 to $x = L$. We have:

$$\int_0^L \left(\sum_{n=0}^{\infty} D_n \cos \lambda_n x\right) \cos \lambda_m x \, dx = \int_0^L \big(c(x,\, 0) - v(x)\big) \cos \lambda_m x \, dx$$

Use the conclusion below:

$$\int_0^L \cos \lambda_n x \cos \lambda_m x \, dx = \begin{cases} 0, n \neq m \\ B, n = m \end{cases}$$

a) Try to calculate the value of B;

b) Let $n = 0$, calculate D_0;

c) If $n > 0$, calculate the value of the integral $\int_0^L \big(c(x,\, 0) - v(x)\big) \cos \lambda_m x \, dx$, and show that if $n > 0$ and n is even, $D_n = 0$; (**Hint**: you might find this integral useful: $\int x \cos x \, dx = x \sin x + \cos x + C$)

d) Calculate he values for $D_{2m+1}, m = 0, 1, 2 \ldots$

5. Summarize the conclusions you reached by solving the problems above. Write down the final answer of the solution for the diffusion equation.