ICFP – Soft Matter

Diffusio-osmosis in a boron-nitride nanotube – Solution

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1 Charge distribution

1. The Debye length for an electrolyte containing several species with charge q_i with concentration C_i is

$$\lambda_D = \sqrt{\frac{k_B T \epsilon_w}{\sum_i q_i^2 C_i}}. \tag{1}$$

For a symmetric electrolyte there are two species with $q_+ = -q_- = e$ and $C_+ = C_- = C$, hence

$$\lambda_D = \sqrt{\frac{k_B T \epsilon_w}{2e^2 C}}. \tag{2}$$

With the given values, we get $\lambda_D \simeq 3$ nm. Since $\lambda_D \ll R$, we can consider the wall of the nanotube as planar.

2. We consider charged species with charge q_i and density $C_{i,\infty}$ (far from any disturbance). Then at equilibrium in a potential $\psi(\boldsymbol{r})$ they adopt a Boltzmann distribution [3]

$$C_i(\boldsymbol{r}) = C_{i,\infty} \exp\left(-\frac{q_i \psi(\boldsymbol{r})}{T}\right). \tag{3}$$

In turn, these charges affect the potential through the Poisson equation:

$$\epsilon \nabla^2 \psi(\boldsymbol{r}) = -\sum_i q_i C_i(\boldsymbol{r}) = -\sum_i q_i C_{i,\infty} \exp\left(-\frac{q_i \psi(\boldsymbol{r})}{T}\right). \tag{4}$$

In a symmetric binary electrolyte where $q_+ = -q_- = e$ and $C_{+,\infty} = C_{-,\infty} = C_\infty$, it takes the form

$$\epsilon \nabla^2 \psi(\boldsymbol{r}) = 2eC_\infty \sinh\left(\frac{e\psi(\boldsymbol{r})}{T}\right). \tag{5}$$

Introducing the rescaled potential $\Psi(\boldsymbol{r}) = e\psi(\boldsymbol{r})/T$ and using the Debye length (2), the equation reads

$$\lambda_D^2 \nabla^2 \Psi(\boldsymbol{r}) = \sinh(\Psi(\boldsymbol{r})). \tag{6}$$

We can even use the Debye length as our unit length, leading to

$$\nabla^2 \Psi(\boldsymbol{r}) = \sinh(\Psi(\boldsymbol{r})). \tag{7}$$

We now solve Eq. (7) at an infinite plane located at $z = 0$:

$$\Psi''(z) = \sinh(\Psi(z)). \tag{8}$$

The solution to this equation is (App. A), reintroducing the Debye length:

$$\tanh\left(\frac{\Psi(z)}{4}\right) = \tanh\left(\frac{\Psi(0)}{4}\right) \exp\left(-\frac{z}{\lambda_D}\right). \tag{9}$$

3. To relate the surface potential $\psi_s = \psi(0)$ to the surface charge Σ, we use the fact that the surface charge should be completely screened by counter-ions, hence

$$\Sigma = -e \int_0^\infty [C_+(z) - C_-(z)] \mathrm{d}z = \epsilon \int_0^\infty \partial_z^2 \psi(z) \mathrm{d}z = -\epsilon \partial_z \psi(0) = \frac{2\epsilon T}{e\lambda_D} \sinh\left(\frac{e\psi_s}{2T}\right). \tag{10}$$

4. Assuming that the system is globally neutral, $\sum_i q_i C_{i,\infty} = 0$, if the rescaled potential is small we can make the Debye-Hückel approximation: we linearize the exponentials in Eq. (4) to get

$$\epsilon \nabla^2 \psi(\boldsymbol{r}) = \sum_i \frac{q_i^2 C_{i,\infty}}{T} \psi(\boldsymbol{r}). \tag{11}$$

With the Debye length (1), it reads

$$\lambda_D^2 \nabla^2 \psi(\boldsymbol{r}) = \psi(\boldsymbol{r}). \tag{12}$$

This is the Debye-Hückel equation.

At a planar wall, the solution of the Debye-Hückel equation (12) is

$$\psi(z) = \psi(0) \exp\left(-\frac{z}{\lambda_D}\right), \tag{13}$$

which coincides with the expansion of Eq. (9) for a symmetric electrolyte.

In this limit, the relation (10) between the surface charge and the surface potential is

$$\Sigma = \frac{\epsilon \psi_s}{\lambda_D}. \tag{14}$$

We use this expression to evaluate if the reduced potential at the surface is small:

$$\frac{e\psi_s}{T} = \frac{e\lambda_D \Sigma}{\epsilon T} \simeq 170; \tag{15}$$

this is not small, hence we cannot use the Debye-Hückel limit.

2 Flow

5. In the Stokes equation, there is no inertia so that the sum of the volumic forces should be zero. The first term represents the viscosity, the second is the effect of pressure, and the third is the electrostatic force.

6. The incompressibility condition reads $\nabla \cdot \boldsymbol{v}(\boldsymbol{r}) = 0$, or $\partial_x v_x + \partial_z v_z = 0$. Since $\partial_x \sim 1/L$ while $\partial_z \sim 1/\lambda_D$, $v_z \ll v_x$.

7. For a simple salt, using the Boltzmann equation,

$$\sum_i q_i C_i(\boldsymbol{r}) = -2eC_\infty \sinh\left(\frac{e\psi(\boldsymbol{r})}{T}\right) \simeq -\frac{2e^2 C_\infty}{T} \psi(\boldsymbol{r}) \tag{16}$$

to the lowest order in the potential. The Stokes equation then reads

$$0 = \eta \nabla^2 \boldsymbol{v}(\boldsymbol{r}) - \nabla p(\boldsymbol{r}) + \frac{2e^2 C_\infty}{T} \psi(\boldsymbol{r}) \nabla \psi(\boldsymbol{r}). \tag{17}$$

8. Projecting the Stokes equation along z, we get

$$\partial_z p = \frac{2e^2 C_\infty}{T} \psi \partial_z \psi = \frac{e^2 C_\infty}{T} \partial_z \left(\psi^2\right). \tag{18}$$

Integrating with $\lim_{z\to\infty} p(x,z) = 0$, we get

$$p(x,z) = \frac{e^2 C_\infty(x)}{T} \psi(x,z)^2. \tag{19}$$

9. Projecting along x, we get

$$0 = \eta\partial_z^2 v_x - \partial_x p + \frac{2e^2}{T} C_\infty(x)\psi\partial_x\psi. \tag{20}$$

Using the expression for the pressure, we arrive at

$$0 = \eta\partial_z^2 v_x - \frac{e^2}{T}\psi(x,z)^2\partial_x C_\infty(x). \tag{21}$$

Using that $\psi(x,z) = \psi_s \exp(-z/\lambda_D)$ and a no slip boundary condition, we get after integration

$$v_x(z) = \frac{\epsilon C'_\infty \psi_s^2}{8\eta C_\infty}\left(\mathrm{e}^{-2z/\lambda_D} - 1\right). \tag{22}$$

3 Electric current

10. As the electrolyte is neutral in the bulk (far from the plate), the flow does not generate any current. However, since there is a concentration gradient in the bulk, there is a diffusive flux of ions. If the cations and anions do not have the same diffusion coefficient, this flux induces an electric current.

11. We define the electric current by an integration on z:

$$I_{\mathrm{DO}} = 2\pi R\int_0^\infty e(C_+ - C_-)v_x \mathrm{d}z = -2\pi R \times \frac{2e^2 C_\infty}{T}\int_0^\infty \psi(z)v_x(z)\mathrm{d}z. \tag{23}$$

Using the expressions above, we get

$$I_{\mathrm{DO}} = 2\pi R \times \frac{\epsilon^{3/2} e C'_\infty}{6\sqrt{2}\eta T^{1/2} C_\infty^{1/2}}\psi_s^3 = 2\pi R \times \frac{T C'_\infty}{24\eta e^2 C_\infty^2}\Sigma^3. \tag{24}$$

12. If $e\psi_s/T \gg 1$, then using the surface charge (Eq. (10)), we can write the current as

$$I = \frac{2\pi R}{L}\frac{\epsilon T^2 \Sigma}{\eta e^2}\Delta \log(C_\infty). \tag{25}$$

On the other hand, if $e\psi_s/T \ll 1$, the current is proportional to $\psi_s^3 \propto \Sigma^3$: it decays very fast for weak surface charges.

13. The density of nanotubes in the membrane is proportional to $1/R^2$, hence the current per unit area is proportional to $1/R$: the thinner the nanotubes, the higher the current.

A Solution of the Poisson-Boltzmann equation at a plane

Here we solve

$$v''(z) = \sinh(v(z)). \tag{26}$$

We assume that the potential is positive at $z = 0$ and decreases to 0 at infinity.

Multiplying by v' and integrating we get

$$\frac{v'^2}{2} = \cosh(v) - 1, \tag{27}$$

where the integration constant has been chosen so that $v \to 0$ and $v' \to 0$ as $z \to \infty$. Now we use

$$\cosh(v) - 1 = 2\sinh\left(\frac{v}{2}\right)^2. \tag{28}$$

Taking the square root and assuming that $v' < 0$, we have

$$v' = -2\sinh\left(\frac{v}{2}\right) = -4\sinh\left(\frac{v}{4}\right)\cosh\left(\frac{v}{4}\right). \tag{29}$$

Dividing both sides by $\cosh(v/4)^2$, and using that $\tanh' = 1/\cosh^2$, we get

$$\tanh\left(\frac{v}{4}\right)' = -\tanh\left(\frac{v}{4}\right), \tag{30}$$

from which we deduce

$$\tanh\left(\frac{v(z)}{4}\right) = \tanh\left(\frac{v(0)}{4}\right)\exp(-z). \tag{31}$$

B Exact solution for the flow and the diffusio-osmosis current

In this appendix we give the exact solutions (without the Debye-Hückel approximation) of sections 2 and 3.

B.1 Flow

The Stokes equation is

$$0 = \eta\nabla^2 \boldsymbol{v}(\boldsymbol{r}) - \nabla p(\boldsymbol{r}) + 2eC_\infty \sinh\left(\frac{e\psi(\boldsymbol{r})}{T}\right)\nabla\psi(\boldsymbol{r}). \tag{32}$$

Projecting the Stokes equation along z, we get

$$\partial_z p = 2eC_\infty \sinh\left(\frac{e\psi}{T}\right)\partial_z\psi = \frac{e^2 C_\infty}{T}\partial_z\left(\psi^2\right). \tag{33}$$

Integrating, we get

$$p(x,z) - p_\infty(x) = 2TC_\infty(x)\left[\cosh\left(\frac{e\psi(x,z)}{T}\right) - 1\right]. \tag{34}$$

Projecting along x, we get

$$0 = \eta\partial_z^2 v_x - \partial_x p + 2TC_\infty(x)\sinh\left(\frac{e\psi(\boldsymbol{r})}{T}\right)\partial_x\psi. \tag{35}$$

Using the expression for the pressure, we arrive at

$$0 = \eta\partial_z^2 v_x - \partial_x p_\infty - 2T\partial_x C_\infty(x)\left[\cosh\left(\frac{e\psi(x,z)}{T}\right) - 1\right]. \tag{36}$$

Taking the limit $z\to\infty$, we see that $\partial_x p_\infty$ should vanish, hence

$$\eta\partial_z^2 v_x = 2TC'_\infty\left[\cosh\left(\frac{e\psi(x,z)}{T}\right) - 1\right]. \tag{37}$$

In order to compute $v_x(z)$ from Eq. (37), we use the solution (9) for the potential. First, we use

$$\cosh\left(\frac{eV}{T}\right) - 1 = 8\cosh\left(\frac{eV}{4T}\right)^2\sinh\left(\frac{eV}{4T}\right)^2 = \frac{8\gamma^2 \mathrm{e}^{-2z/\lambda_D}}{\left(1-\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)^2} = -\partial_z^2\left[2\lambda_D^2\log\left(1-\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)\right], \tag{38}$$

where we have used that $\cosh^2\sinh^2 = \tanh^2/\left(1-\tanh^2\right)^2$ and defined

$$\gamma = \tanh\left(\frac{eV_s}{4T}\right), \tag{39}$$

where V_s is the surface potential. Using this relation in Eq. (37) and integrating with a no slip boundary condition, we get

$$v_x(x,z) = \frac{4TC'_\infty\lambda_D^2}{\eta}\left[\log\left(1-\gamma^2\right) - \log\left(1-\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)\right] \tag{40}$$

With the expression of the Debye length,

$$v_x(x,z) = \frac{2T^2\epsilon}{\eta e^2}\log(C_\infty)'\left[\log\left(1-\gamma^2\right) - \log\left(1-\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)\right] \tag{41}$$

Far from the surface,

$$v_x(x,\infty) = \frac{2T^2\epsilon}{\eta e^2}\log(C_\infty)'\log\left(1-\gamma^2\right). \tag{42}$$

B.2 Diffusio-osmosis current

We define the electric current by an integration on z:

$$I = \int_0^\infty e(C_+ - C_-)v_x \mathrm{d}z. \tag{43}$$

We then use $C_+ - C_- = -2C_\infty \sinh(eV/T)$, with

$$\sinh\left(\frac{eV}{T}\right) = 4\sinh\left(\frac{eV}{4T}\right)\cosh\left(\frac{eV}{4T}\right)\left[2\cosh\left(\frac{eV}{4T}\right)^2 - 1\right] = \frac{4\gamma \mathrm{e}^{-z/\lambda_D}\left(1+\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)}{\left(1-\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)^2}, \tag{44}$$

where we have used the solution (9). Using now the velocity profile (40), we arrive at

$$I = -32\frac{eTC_\infty C'_\infty \lambda_D^2}{\eta}\int_0^\infty \mathrm{d}z \frac{\gamma \mathrm{e}^{-z/\lambda_D}\left(1+\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)}{\left(1-\gamma^2\mathrm{e}^{-2z/\lambda_D}\right)^2}\log\left(\frac{1-\gamma^2}{1-\gamma^2\mathrm{e}^{-2z/\lambda_D}}\right) \tag{45}$$

$$= -32\frac{eTC_\infty C'_\infty \lambda_D^3}{\eta}\int_0^\gamma \mathrm{d}q \frac{1+q^2}{(1-q^2)^2}\log\left(\frac{1-\gamma^2}{1-q^2}\right). \tag{46}$$

Mathematica gives for the integral

$$\int_0^\gamma \mathrm{d}q \frac{1+q^2}{(1-q^2)^2}\log\left(\frac{1-\gamma^2}{1-q^2}\right) = \tanh^{-1}(\gamma) - \frac{\gamma}{1-\gamma^2} = \frac{eV_s}{4T}\left[1 - \frac{2T}{eV_s}\sinh\left(\frac{eV_s}{2T}\right)\right]. \tag{47}$$

Finally, the current in a nanotube with radius R is given by

$$I = 2\pi R \times 8\frac{e^2 C_\infty C'_\infty V_s \lambda_D^3}{\eta}\left[\frac{2T}{eV_s}\sinh\left(\frac{eV_s}{2T}\right) - 1\right]. \tag{48}$$

References

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