ICFP – Soft Matter

Diffusio-osmosis in a boron-nitride nanotube

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Diffusio-osmosis notably refers to electrical transport induced by salinity gradients [1, 2]. Here, we study this phenomenon and apply it to boron-nitride nanotubes (BNNT), which could ultimately be used to convert the salinity difference between fresh water and sea water into electric energy.

Boron-nitride nanotubes are charged, and their surface charge is screened by counter-ions. First, we use the Poisson-Boltzmann equation to determine the density profile of counter-ions close to the surface of the nanotube; the thickness of the cloud of counter-ions is given by the Debye length. The Debye length depends on the salt concentration, hence a gradient of salt concentration results in a gradient of Debye length, and hence a gradient of electric potential parallel to the surface, giving rise to a current. The second step is to use the Stokes equation to describe this flow. Finally, we compute the electric current generated by this flow.

1 Charge distribution

1. Recall the expression of the Debye length λ_D in an electrolyte. Estimate its value at room temperature for a simple salt at concentration $C = 10^{-2}$ M. We give $k_B T \simeq 4 \cdot 10^{-21}$ J at room temperature, $e \simeq 1.6 \cdot 10^{-19}$ C, the Avogadro number $\mathcal{N}_A \simeq 6 \cdot 10^{23}$ and the permittivity of water $\epsilon_w \simeq 7 \cdot 10^{-10}$ Fm^{-1}. Compare the Debye length to the radius of the BNNTs, $R = 15\,\mathrm{nm}$ to $40\,\mathrm{nm}$, and explain why we can consider the wall of the nanotube as planar. In the following we set $k_B = 1$ so that the thermal energy is T.

2. * Derive the Poisson-Boltzmann equation for the electrostatic potential $\psi(\boldsymbol{r})$ and specialize it to a symmetric electrolyte [3]. Then solve it in a planar geometry. We admit that the solution of $u''(z) = \sinh(u(z))$ is $\tanh(u(z)/4) = \tanh(u(0)/4)\exp(-z)$.

3. * Relate the surface charge Σ to the surface potential ψ_s.

4. * Discuss the Debye-Hückel limit in the previous questions. The BNNTs have a very large electric charge, $\Sigma \simeq 1$ Cm^{-2}; can we use the Debye-Hückel limit?

2 Flow

5. Comment the different terms of the Stokes equation [1]

$$0 = \eta \nabla^2 \boldsymbol{v}(\boldsymbol{r}) - \nabla p(\boldsymbol{r}) - \sum_i q_i C_i(\boldsymbol{r}) \nabla \psi(\boldsymbol{r}), \tag{1}$$

where q_i and $C_i(\boldsymbol{r})$ are the charge and density of the species i.

6. Write the incompressibility condition. Given that the scale of the variation of the different quantities along the nanotube are given by its length, $L \simeq 1$ µm, explain why the normal velocity component, v_z, is negligible with respect to the tangential component v_x; we neglect it in the following.

7. Write the Stokes equation for a simple salt and use the Boltzmann equation to eliminate the concentrations $C_i(\boldsymbol{r})$. Furthermore, in order to simplify the calculations we restrict ourselves to the lowest order in the surface potential ψ_s (we take the Debye-Hückel limit).

8. Project the Stokes equation on the direction normal to the wall, assuming that $\lim_{z\to\infty} p(x, z) = 0$, to show that the pressure profile is given by

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

9. * Project the Stokes equation along the wall and integrate the resulting equation to obtain $v_x(z)$ for a concentration gradient C'_∞, using a slip boundary condition at the wall and the fact that the velocity $v_x(z)$ goes to a constant far from the wall.

3 Electric current

10. Does the flow computed in the previous section induce an electric current in the bulk? Can the difference in diffusivity between the anions and cations induce an electric current in the bulk? Here we assume that they have the same diffusivity.

11. * Compute the diffusio-osmotic electric current in the BNNT induced by the flow,

$$I_{\mathrm{DO}} = 2\pi R \int_0^\infty e[C_+(z) - C_-(z)]v_x(z)\mathrm{d}z. \tag{3}$$

The exact expression is

$$I_{\mathrm{DO}} = 2\pi R \times \frac{2\sqrt{2}(\epsilon T)^{3/2}\psi_s C'_\infty}{e\eta C_\infty^{1/2}}\left[\frac{2T}{e\psi_s}\sinh\left(\frac{e\psi_s}{2T}\right) - 1\right]. \tag{4}$$

12. How does the diffusio-osmotic electric current scale in the limit of small and large surface charge?

13. What is the interest of using such nanotubes in a membrane to convert osmotic into electric energy?

References

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