Cell - Foreign Particle Interaction

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1 Introduction

The cell is the base building block of life which all living organisms possess. The number of cells which make up a living organism range from one to many billions, as is the case with humans. Cells come in many different types and serve a wide variety of functions. All of them share some common characteristics including having an outer membrane and a nucleus containing DNA and RNA, the ability to create protiens, and the ability to replicate. A sample diagram of a cell is shown in Figure 1.

The cell consists of many different organelles, which each serve some function to the cell, surrounded by an electrolyte solution and contained by a cell membrane.

In this work, the two most important aspects of the cell are the cell membrane and the electrolyte solution which it encloses. The cell membrane serves as the boundary and regulates the intake (endocytosis) and expulsion (exocytosis) of particles from the cell. It contains many different parts including ion channels and pumps, proteins and lipid molecules.

A schematic of a lipid molecule is shown in Figure 2. Lipid molecules are amphiphiles, which means that they have a dual affinity to water, that consist of a hydrophobic tail connected to a polar hydrophillic head group. The head group may have either positive or negative charge depending on its specific chemical structure and both types can occur in the same cellular membrane. When placed in water at a sufficient concentration, the lipid molecules will arrange in such a way to minimize the tails groups contact area with the water and vice versa for the head.

For a cell membrane, the lipid molecules form a bilayer, as shown in figure 2. The solution directly inside or outside the cell consists of an electrolyte, which is an electrically conducting medium. The electrolyte contains both positive and negative ions in water. The ions present typically include sodium(Na^+), potassium(K^+), calcium(Ca^{2+}), chloride(Cl^-), bicarbonate($HCO_3{}^-$), and phosphate($PO_4{}^{3-}$).

The concentration of ions on either side of the cell membrane is generally different, which leads to an electrical potential difference across the membrane. This potential difference has been experimentally measured to be approximately 70 mV. The charge outside the cell is net positive and the charge inside is net negative. It's known that

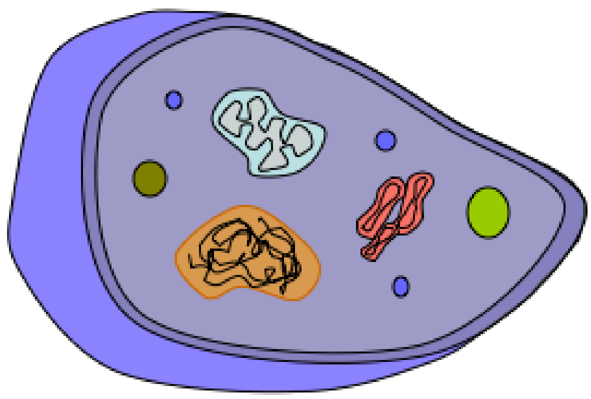

Figure 1: A typical biological cell.

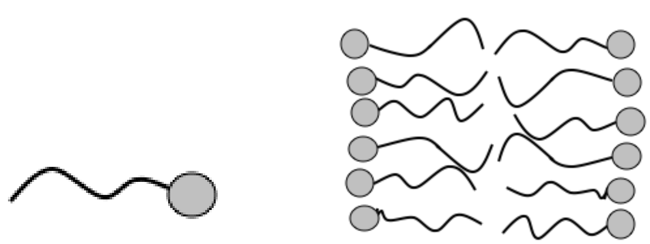

Figure 2: a) The shape of a lipid molecule. b) The bilayer structure of a cell membrane.

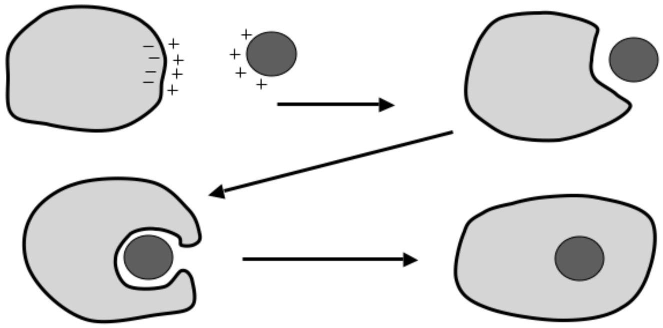

Figure 3: Schematic of the endocytosis process by which particles are engulfed by a cell.

there is more positive charge than negative. The cell uses active transport of ions across the membrane to maintain this potential difference. The transport of particles across the cell membrane is the main thrust of this work. Not only are ions transported across the membrane, but also protiens and foreign particles.

Foreign particles can include drug delivery devices and medical implant debris. These foreign particles generally hinder the functions of the cell. It is thus important to better understand how these particles get inside the cell.

A general schematic of the endocytosis of a foreign particle is shown in Figure 3. The foreign particle generally has a net positive charge. The particle initially approaches the cell membrane which causes the membrane to deform inwards. As it moves further inside, the cell membrane eventually envelopes the particle and breaks off, pulling the particle into the interior of the cell. The forces which drive endocytosis of the particle include electrodynamic interactions, thermal interactions, and osmotic pressure. This process is not well understood and is the subject of this work.

2 Background

2.1 Electrostatics

From electrostatic theory we know that the behavior of an electric potential ψ satisfies Poisson's equation

$$-\epsilon\Delta\psi = \zeta, \tag{1}$$

where ζ is the total electric charge per unit volume. The electric field is then the gradient of this potential.

$$\mathbf{E} = -\nabla\psi \tag{2}$$

Classical problems of electrostatics require the solution of Poisson's equation for a given ζ and it's boundary conditions. However, further complexity is added if the charges are free to move, as ζ becomes a function of ψ.

In order to determine a unique solution, equation (1) must be coupled to appropriate boundary conditions. For the case of an interface joining media $i = 1, 2$ with dielectric constants ϵ_i and outer unit normals $\mathbf{n}_i$, Maxwell's equations imply that the normal component of $\epsilon_i \mathbf{E}_i$ has a discontinuity jump of σ and the tangential component is continuous. If σ is the charge density per unit area then

$$\sigma = \epsilon_1 \mathbf{E}_1 \cdot \mathbf{n}_1 + \epsilon_2 \mathbf{E}_2 \cdot \mathbf{n}_2, \tag{3}$$

$$\psi_1 = \psi_2, \text{ at the interface} \tag{4}$$

involving the surface charge density σ. Alternatively, using (2) we could write this equation in terms of the potential as

$$\epsilon_1 \frac{\partial \psi}{\partial n_1} + \epsilon_2 \frac{\partial \psi}{\partial n_2} = -\sigma. \tag{5}$$

In the case of a conductor, the interior electric field is zero, so $\epsilon = 0$.

2.2 Boltzmann's Distribution in Electrolyte Media

An electrolyte consists of an aqueous solution of oppositely charged ions, such as NaCl, which dissociates in solution to Na^+ and Cl^-. These ions are free to move under the influence of an electric field, so the electrolyte can often be considered a conductor. However at short length scales, the thermal motion of the ions becomes significant and electric fields may be present. In this case, thermodynamic equilibrium is reached when the concentration of an ion species of charge q is such that the chemical potential,

$$\mu = q\psi + kT \log \rho, \tag{6}$$

is constant. Consequently, if the concentration is known to be ρ^∞ in the far field, where the electric potential approaches ψ^∞, the equilibrium concentration at any point is related to ψ by

$$\rho = \rho^\infty e^{-\frac{q(\psi - \psi^\infty)}{kT}}. \tag{7}$$

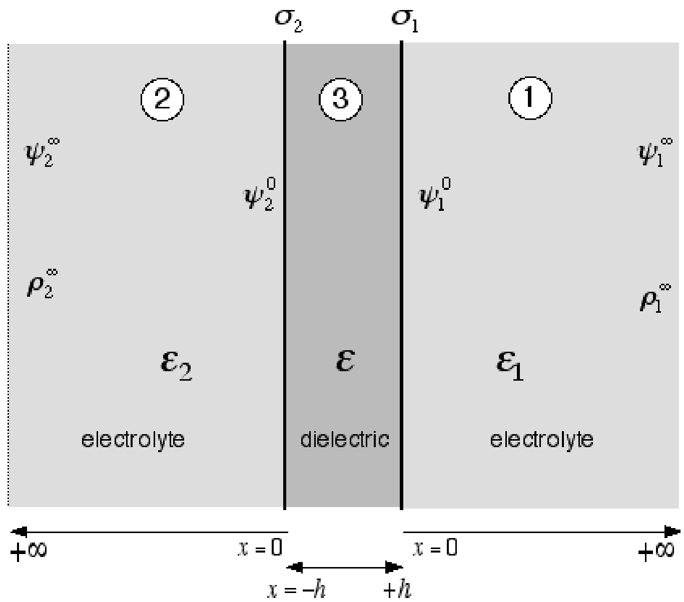

Figure 4: In Model I a bilayer is represented by two charged planes with a dielectric inside and two electrolyte solutions outside.

Here k is Boltzmann's constant and T is the temperature of the solution. This equation expresses the balance between the electric force and thermal motion. Combining equations (6) and (7) yields the Poisson-Boltzmann equation

$$-\epsilon \Delta \psi = \Sigma_j q_j \rho_j^\infty e^{-\frac{q_j(\psi - \psi^\infty)}{kT}}, \tag{8}$$

for an electrolyte containing ions of charge q_j. In this work we are concerned with electrolytes containing two charges $\pm q$, in which case the Poisson-Boltzmann equation can be written

$$\epsilon \Delta \psi = 2q\rho^\infty \sinh \frac{q(\psi - \psi^\infty)}{kT} \tag{9}$$

assuming an appropriate ρ^∞ and ψ^∞ are known.

3 Problem I: A Membrane in Solution

As a first model, we represent a cell membrane by two charged films separated by a length $2h$ of dielectric material, corresponding to the ionized headgroups and nonpolar tails of the membrane lipids, respectively.

As shown in figure (4), regions 1 and 2 contain a z - z electrolyte solution with electric permittivities ϵ_1 and ϵ_2 respectively. Region 3 is a pure dielectric medium with electric permittivity ϵ. Interfaces 2 - 3 and 3 - 1 are considered to have charge densities σ_2 and σ_1 respectively. We want to determine the ion charge distribution in media

1 and 2, which will involve solving equation (9) in media 1 and 2 and equation (1) in medium 3, together with (3) at both interfaces. According to the simmetry of the problem this becomes of one dimensional type, then equation (9) in media 2 and 1 takes the following form,

$$
\begin{aligned}
-\epsilon_2 \frac{d^2\psi_2}{dx^2} &= \rho_2^\infty q^+ (e^{\frac{-q^+(\psi_2-\psi_2^\infty)}{kT}} - e^{\frac{q^+(\psi_2-\psi_2^\infty)}{kT}}) \\
-\epsilon_1 \frac{d^2\psi_1}{dx^2} &= \rho_1^\infty q^+ (e^{\frac{-q^+(\psi_1-\psi_1^\infty)}{kT}} - e^{\frac{q^+(\psi_1-\psi_1^\infty)}{kT}})
\end{aligned}
\tag{10}
$$

where we have assumed the electrolyte media in both regions consist of opposite charges $\pm q$ with far - field concentrations ρ_1^∞ and ρ_2^∞. From equation (1) we know that ψ in medium 3 is given by

$$\psi_3(x) = Ax + B \tag{11}$$

where A and B are constants to be determined. In order to complete our model we'll state some boundary bonditions. As we can fix any point to be at potential 0, we set $\psi_3(0) = 0$. Considering (2), (5) and (11) we obtain the following relations on the interfaces 3 - 1 and 2 - 3

$$-\epsilon A + \epsilon_1 \frac{d\psi_1}{dx}|_{x=0} = -\sigma_1 \tag{12}$$

$$-\epsilon A + \epsilon_2 \frac{d\psi_2}{dx}|_{x=0} = -\sigma_2 \tag{13}$$

Adding and substracting equations (12) and (13), we obtain

$$-\epsilon_1 \frac{d\psi_1}{dx} - \epsilon_2 \frac{d\psi_2}{dx} + 2\epsilon A = \sigma_1 - \sigma_2 \tag{14}$$

$$-\epsilon_2 \frac{d\psi_2}{dx} + \epsilon \frac{d\psi_1}{dx} = -(\sigma_1 + \sigma_2). \tag{15}$$

and from the continuity of the electrostatic potential $\psi_1(h) = \psi_3(h)$, $\psi_2(-h) = \psi_3(-h)$ we obtain the following value of A

$$A = \frac{\psi_1(0) - \psi_2(0)}{2h} \tag{16}$$

at which equation (14) becomes

$$\epsilon\psi_1 - \epsilon\psi_2 - h\epsilon_2 \frac{d\psi_2}{dx}(-h) - h\epsilon_1 \frac{d\psi_1}{dx}(h) = h(\sigma_1 - \sigma_2). \tag{17}$$

At this point we observe that boundary conditions (17) and (15) imply that the net charge in the whole domain is zero, hence if $I_1 = (-\infty, -h)$, $I_2 = (-h, h)$, $I_3 = (h, \infty)$ then

$$\begin{aligned}
\int_R \zeta + \sigma_1 + \sigma_2 &= \int_{I_1} \zeta + \int_{I_2} \zeta + \int_{I_3} \zeta \\
&= -\epsilon_2 \int_{I_1} \frac{d^2\psi_2}{dx^2} - \epsilon_1 \int_{I_3} \frac{d^2\psi_1}{dx^2} + \sigma_1 + \sigma_2 \\
&= -\epsilon_2 [\frac{d\psi_2}{dx}(-h) - \frac{d\psi_2}{dx}(-\infty)] - \epsilon_1 [\frac{d\psi_1}{dx}(\infty) - \frac{d\psi_1}{dx}(h)] + \sigma_1 + \sigma_2 \\
&= -\epsilon_2 \frac{d\psi_2}{dx}(-h) + \epsilon_1 \frac{d\psi_1}{dx}(h) + \sigma_1 + \sigma_2 \\
&= 0,
\end{aligned}$$

where (1), (15) and condition $\psi \to \psi_i^\infty$ as $|x| \to \infty$ were applied. We also note that after decoupling medium 3 we have only two boundary conditions, equations (15) and (17), coupling the second order equations in media 1 and 2. While we anticipate a single degree of freedom since adding a constant to the electric potential everywhere leaves the physics unchanged, we still need one more condition in order to make the system well-posed. Lets analyze first what happens with the charge density in medium 1. From (7) we know that $\rho_1^+ = \rho_1^\infty e^{-\frac{q(\psi_1 - \psi_1^\infty)}{kT}}$ and $\rho_1^- = \rho_1^\infty e^{+\frac{q(\psi_1 - \psi_1^\infty)}{kT}}$, then after using $q(\rho_1^- - \rho_1^+) = -\epsilon_1 \frac{d^2\psi_1}{dx^2}$ we obtain

$$\frac{d(\rho_1^+ + \rho_1^-))}{dx} = -\frac{q\epsilon_1}{2kT} \frac{d}{dx} (\frac{d\psi}{dx})^2.$$

Integrating the previous equation on $(0, \infty)$ we obtain the following boundary condition

$$(\frac{d\psi_1}{dx})^2(0) = \frac{8\rho_1^\infty kT}{\epsilon_1} \sinh^2(q(\psi_1 - \psi_1^\infty)), \tag{18}$$

similarly for medium 2 we obtain

$$(\frac{d\psi_2}{dx})^2(0) = \frac{8\rho_1^\infty kT}{\epsilon_2} \sinh^2(q(\psi_2 - \psi_2^\infty)), \tag{19}$$

finally the last condition is obtained from the *Nerst Potential*[3] equation which applied to our situation takes the following form

$$\psi_2^\infty - \psi_1^\infty = \frac{kT}{F} \log(\frac{\rho_1^\infty}{\rho_2^\infty}).$$

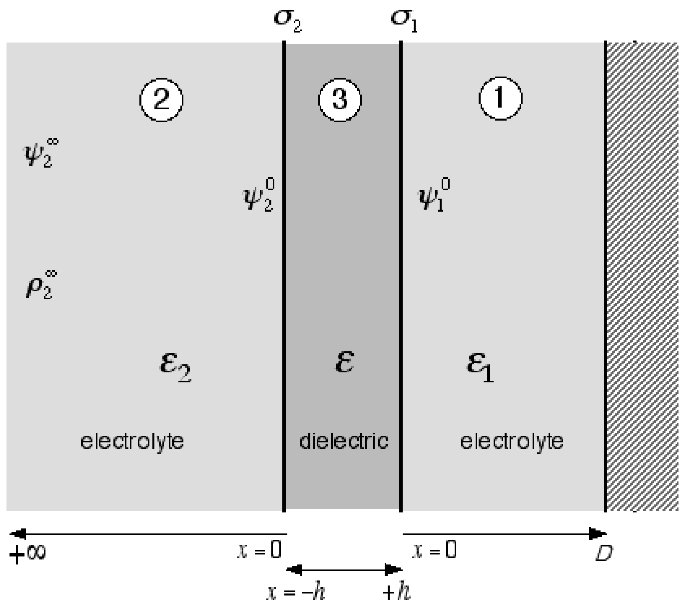

Figure 5: Model II, a large particle.

4 Problem II: A Planar Particle

We next consider a one dimensional model of a foreign particle interaction, in which the particle is represented by a charged plane located at $x = D$. This may be realistic if the separation between the particle and cell is small compared to both of their dimensions and we are concerned with the solution only in the vicinity of minimum separation. Denoting medium 1 by $h < x < D$ and media 2 and 3 as before, we can again apply the boundary conditions 15 and 17 at the two membrane interfaces, and again seek solutions to equation 9. In this situation, however, an additional assumption must be made about the boundary condition at $x + D$. Equation 3 states that we must have some knowledge of the electric field and permittivity inside the particle, which in reality will depend on the large-scale geometry which we have ignored. However, with the tentative condition

$$\frac{d\psi}{dx}|_{x=D^+} = 0 \tag{20}$$

we may proceed. There is also a subtlety in the way equation 7, and therefore the Poisson-Boltzmann equation, is applied in region 1. The point at which $\psi = \psi_1^\infty$ and $\rho^+ = \rho^- = \rho_1^\infty$ no longer occurs in the domain of the problem. We still expect such a point to exist, far from the cell and the charged particle, and we also expect this point to have the same chemical potential as region 1. Therefore, we define ρ_1^∞ and ψ_1^∞ as the concentration and electric potential at this unspecified point, and assume equation 7 holds throughout region 1 for these values. Additionally, we determine the cross-membrane potential $\psi_1^\infty - \psi_2^\infty$ from the Nernst potential as before. Since ψ_1^∞ appears

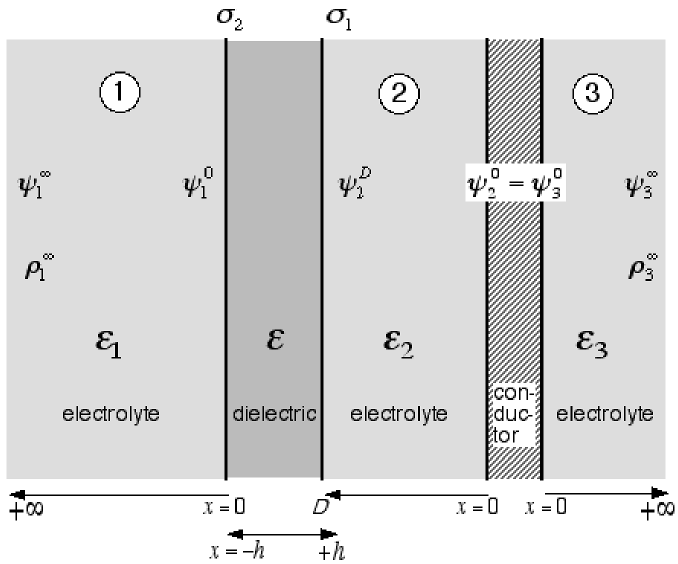

Figure 6: Model III, a particle of finite extent.

in the differential equation for region 1 rather than the solution, this last assumption should not be considered a boundary condition, and we again have three boundary conditions for two second-order equations, leaving the expected one degree of freedom.

Finding a solution to this system is considerably more complicated than the previous case. A closed-form solution to equation 9 in region 1 exists in terms of the elliptic integral, however this does not necessarily make the problem of solving the boundary conditions simple. Finding the correct solution would again depend on solving a set of nonlinear algebraic equations involving this integral. Alternatively, the problem could be solved numerically as a two-point boundary value problem in region 1, with the nonlinear boundary condition at $x = h$ involving the known (in terms of $\psi_1(h)$ and $\psi_1'(h)$) solution in region 2 computed in the previous model. In either case, this model is limited in its realism by the assumptions on the electric field inside the particle.

5 Problem III: A Finite Conducting Particle

To consider a conducting particle of finite extent, we assume an electrolyte (medium 3) beyond the particle which is in thermal equilibrium with medium 2, as shown in figure 6. Thus the ion concentration

$$\rho_\pm = \rho_3^\infty e^{-\frac{q(\psi - \psi_3^\infty)}{kT}} \tag{21}$$

takes the same form in both regions and the corresponding Poisson-Boltzmann equation

$$\epsilon_i \psi_i'' = 2q\rho_3^\infty \sinh \frac{q\psi_i}{kT} \tag{22}$$

changes only through ϵ. In the shown coordinates, the interface conditions are

$$\epsilon_1\psi_1'(0) + \epsilon A = -\sigma_1 \qquad \epsilon_2\psi_2'(0) = -\sigma_3 \tag{23}$$

$$-\epsilon_2\psi_2'(d) - \epsilon A = -\sigma_2 \qquad \epsilon_3\psi_3'(0) = -\sigma_4 \tag{24}$$

$$\psi_2(d) - \psi_1(0) = 2Ah \qquad \psi_2(0) = \psi_3(0) \tag{25}$$

We take the far-field membrane potential to be $\Delta_\infty = \psi_3^\infty - \psi_1^\infty$. The strength of the charge on the particle must also be specified, either through the potential $\Delta_p = \psi_p - \psi_3^\infty$ or its total charge $\sigma_p = \sigma_3 + \sigma_4$. This is then a total of 8 constraints, to determine 3 second-order solutions. However, 3 of these constraints will be used to determine the unknown values of A, σ_3, and σ_4, so there will be a single freedom representing the arbitrary choice of $\psi = 0$. The boundary conditions are not expressed in terms of the same solution parameters, though, so while the solution is already determined the individual ODE problems remain coupled. Using the fact that

$$\frac{d}{dx}(\rho_2^+ + \rho_2^-) = \frac{2q\rho_3^\infty}{2kT}\frac{d\psi_2}{dx}\sinh\frac{q(\psi_2 - \psi_3^\infty)}{kT} = \frac{\epsilon_2}{kT}\frac{d}{dx}\left(\frac{d\psi_2}{dx}\right)^2,$$

we can integrate from 0 to d and obtain

$$\cosh\frac{q(\psi_2^d - \psi_3^\infty)}{kT} - \cosh\frac{q(\psi_2^0 - \psi_3^\infty)}{kT} = \frac{\epsilon_2}{2kT}\left(\psi_2'(d)^2 - \psi_2'(0)^2\right) \tag{26}$$

as well as

$$(\frac{\partial\psi_1}{\partial x})^2(0) = \frac{8\rho_1^\infty kT}{\epsilon_1}\sinh^2(q(\psi_1 - \psi_1^\infty)) \tag{27}$$

$$(\frac{\partial\psi_3}{\partial x})^2(0) = \frac{8\rho_3^\infty kT}{\epsilon_3}\sinh^2(q(\psi_3 - \psi_3^\infty)). \tag{28}$$

These equations may be used to eliminate three boundary values appearing in the above boundary conditions. However, this still is not sufficient to decouple the problems as was the case earlier, since the boundary conditions in their present form require four different parameters ψ_2^0, ψ_2^d, $\psi_2'(0)$, and $\psi_2'(d)$. This does not mean the problem is underdetermined, as there can only be a two-parameter family of solutions in region 2. We simply cannot determine the boundary values algebraically and decouple the ODE regions. Although it would be convenient to impose another condition on ψ_2 in order to determine these boundary values without solving the ODE's, any such condition must be equivalent to equation 22 to avoid overdetermining the system.

6 Problem IV: Two spheres

In this problem we consider two spheres $S_{r_1}^1$ and $S_{r_2}^2$ separated at a distance $2h$ from their centers, and submerged in a z - z electrolyte solution of permittivity ϵ. Sphere

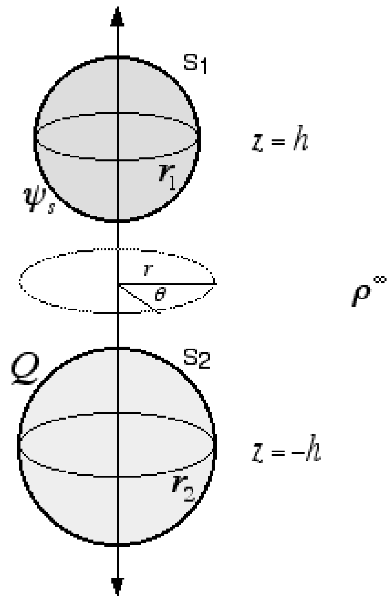

Figure 7: Geometry of problem IV.

$S^1_{r_1}$ is a conductor and sphere $S^2_{r_2}$ is given a fixed charge Q distributed uniformly on its surface. The conducting sphere S_1 here models a cell membrane in which the lipid molecules are able to move to redistribute charge, and the charged sphere S_2 models a nearby particle as described in section 1.1. We have neglected the cytoplasm and the double layer structure of the cell membrane in order to simplify the problem.

According to the geometry of the problem, we decided to work in a cylindrical coordinate system. Both spheres are described as follows

$$\begin{aligned} S_1 &= \{(r,\phi,z) : r^2 + (z-h)^2 \le r_1^2\} \\ S_2 &= \{(r,\phi,z) : r^2 + (z+h)^2 \le r_2^2\} \end{aligned}$$

according to the symmetry of the problem this becomes independent of ϕ, therefore it's a two dimensional problem. Equation (9) takes the following form

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \psi}{\partial r}\right) + \frac{\partial^2 \psi}{\partial z^2} = -\frac{q\rho^\infty}{\epsilon}\left(e^{-\frac{q\psi}{kT}} - e^{\frac{q\psi}{kT}}\right), \quad \text{outside } \left(S^1_{r_1} \cup S^2_{r_2}\right) .$$

The amount of charge both spheres possess is contained in a finite volume, this implies the electrostatic potential must approach a constant value (which we take to be zero) as $|z| \to \infty$ or $r \to \infty$. To complete the boundary conditions we must specify the behaviour of ψ on $\partial S^2_{r_2}$.

Notice that the electric field produced by $S^2_{r_2}$ at $\partial S^2_{r_2}$ behaves like the one produced by a point-charge located at the center of $S^2_{r_2}$ at a distance r_2. After using equation (2) restricted on $\partial S^2_{r_2}$, we obtain the following boundary condition:

$$\frac{\partial \psi}{\partial \eta}|_{\partial S^2_{r_2}} = -\frac{Q}{4\pi\epsilon r_2^2}$$

where $\frac{\partial \psi}{\partial \eta}|_{\partial S^2_{r_2}}$ is the derivative of ψ in the direction normal to $S^2_{r_2}$ at $\partial S^2_{r_2}$. Therefore our model takes the following form:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \psi}{\partial r}\right) + \frac{\partial^2 \psi}{\partial z^2} = -\frac{q\rho^\infty}{\epsilon}\left(e^{-\frac{q\psi}{kT}} - e^{\frac{q\psi}{kT}}\right), \quad \text{outside } (S^1_{r_1} \cup S^2_{r_2}) \ . \tag{29}$$

subject to:

$$\tfrac{\partial \psi}{\partial \eta}|_{\partial S^2_{r_2}} = -\tfrac{Q}{4\pi\epsilon r_2^2} \ , \quad \psi|_{\partial S^1_{r_1}} = \psi_s$$

$$\psi \to 0, \quad as \ |z| \to \infty \ or \ r \to \infty.$$

Deriving an analytical solution for this type of problem is very difficult, inmediate solutions can only be obtained numerically. We suggest the finite element method is a good option by the fact that the boundaries of the domain are non - rectangular.

After solving (29) numerically, the net surface charge distribution on $S^1_{r_1}$ can be calculated from the relation

$$-\frac{\partial \psi}{\partial \eta}|_{S^1_{r_1}} = \frac{\sigma_s}{\epsilon}$$

where σ_s is the net surface charge on $S^1_{r_1}$.

This model could provide good approximations of σ_s when the effects of the membrane can be negligible, maybe when both spheres are far apart. A more precise model can be developed by replacing $S^1_{r_1}$ for a spherical capacitor. The dielectric of the capacitor represents in this case the membrane of the cell. In the case of vacuum, the surface charge on a spherical capacitor is known [7] when is exposed to a constant electric field. For the case of an electrolyte the situation is more complicated, we don't even have a constant electric field in this case.

No model was obtained for the problem spherical capacitor - solid nonconducting sphere, this will be considered for future work.

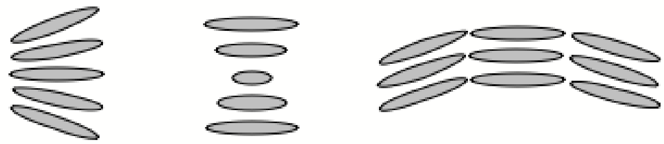

Figure 8: Splay, twist and bend elastic deformations of a liquid crystal. Only the splay is important in this work as it is the type of deformation which the cell membrane experiences as a foreign particle deforms it.

7 Cell Membrane Deformations

In order to include cell membrane deformations into this work, we need to take into account the liquid crystalline nature of the membrane. The long axis of the lipid molecules in the membrane can be described by a vector $\vec{n}$, called the director. The director is defined such that $\vec{n} = -\vec{n}$. In general, the total free energy of a liquid crystal then is given by the Frank-Oseen total free energy

$$F = \frac{1}{2}\int \Big(K_1(\text{div } \vec{n})^2 + K_2(\vec{n}\cdot \text{curl } \vec{n})^2 + K_3(\vec{n}\times \text{curl } \vec{n})^2\Big)\, dV. \tag{30}$$

The free energy contains three terms which denote the three principle distortions possible within the liquid crystal, which are splay, twist, and bend. Each deformation has an associated elastic constant, K_1, K_2, and K_3 respectively. Schematics of these three deformations are shown in figure 8. The splay term will be the most important for this work because it is the type of deformation that the cell experiences as the foreign particle deforms the cell membrane. The equilibrium director configuration can be found by minimizing the total free energy.

If we consider the cell wall to be a two dimensional surface with only splay deformations which encloses a volume, V, we can rewrite the total free energy [8] as

$$F = 2\int \left(\frac{K_1}{r^2} + \lambda\right) d\Lambda + p\int dV \tag{31}$$

In this equation, r is the radius of curvature of the surface, λ is the surface tension, and p is the pressure difference between the two sides of the membrane. It is important to include the surface tension term because the membrane wants to minimize its surface area. The pressure difference term stems from the relative incompressibility of the cell membrane. To determine the equilibrium shape of the cell membrane in the presence of a foreign particle, the liquid crystalline deformation energy must be balanced with the electrostatic and thermodynamic interaction energy contribution from the particle.

APPENDIX A: Mathematical Simplification Of Algebraic System in Double Layer Problems

In order to get a feeling how the algebraic system determines the problem, we end up with finding solution of an algebraic equation in terms of $\psi_1(0)$. For simplicity, we assume that the potential in the middle of the membrane equals to zero. Thus, we have

$$\psi_1(0) + \psi_2(0) = 0$$

Rewrite (12) and (13), substituting $A = \frac{\psi_1(0)-\psi_2(0)}{2h}$

$$\psi_1'(0) = \frac{\epsilon}{2h\epsilon_1}(\psi_1(0) - \psi_2(0)) - \frac{\sigma_1}{\epsilon_1} = \frac{\epsilon}{h\epsilon_1}\psi_1(0) - \frac{\sigma_1}{\epsilon_1} \quad (32)$$

$$\psi_2'(0) = \frac{\epsilon}{2h\epsilon_2}(\psi_1(0) - \psi_2(0)) - \frac{\sigma_2}{\epsilon_2} = -\frac{\epsilon}{h\epsilon_1}\psi_1(0) - \frac{\sigma_2}{\epsilon_2} \quad (33)$$

For convenience, let us use the notation $\Delta\psi^\infty = \psi_1^\infty - \psi_2^\infty$, thus, from Nerst equation $\Delta\psi^\infty = \frac{kT}{F}\log(\frac{\rho_1^\infty}{\rho_2^\infty})$, we have

$$\psi_2(0) - \psi_2^\infty = -\psi_1(0) - \psi_1^\infty + \Delta\psi^\infty$$

Combine with (18) and (19), we can eliminate the $\psi_1'(0)$ and $\psi_2'(0)$, now we have two equations

$$(\frac{\epsilon}{h\epsilon_1}\psi_1(0) - \frac{\sigma_1}{\epsilon_1})^2 = \frac{8\rho_1^\infty kT}{\epsilon_1}\sinh^2(q(\psi_1(0) - \psi_1^\infty)), \quad (34)$$

$$(\frac{\epsilon}{h\epsilon_1}\psi_1(0) + \frac{\sigma_2}{\epsilon_2})^2 = \frac{8\rho_1^\infty kT}{\epsilon_2}\sinh^2(q(-\psi_1(0) - \psi_1^\infty + \Delta\psi^\infty)) \quad (35)$$

Now we have a system of two equation in terms of two unknowns $\psi_1(0)$ and ψ_1^∞.

Intuitively we can solve ψ_1^∞ from the first equation and substitute into the second equation and we have an equation in terms of one unknown. On the other hand, under the assumption that the concentration of electrolyte far away from the membrane are same, we have

$$\mathrm{sign}(\psi_1(0) - \psi_1^\infty) = \mathrm{sign}(\sigma_1 - \sigma_2)$$
$$\mathrm{sign}(\psi_2(0) - \psi_2^\infty) = \mathrm{sign}(\sigma_2 - \sigma_1)$$

Take square root of the two equations, we have an equation of $\psi_1(0)$ as the following

$$\psi_1(0) = \frac{\Delta\psi^\infty}{2} + \mathrm{sign}(\sigma_1 - \sigma_2)(kT/q)(\sinh^{-1}(\sqrt{\frac{\epsilon_1}{8kT\rho_1^\infty}}|\frac{\epsilon}{h\epsilon_1}\psi_1(0) - \frac{\sigma_1}{\epsilon_1}|) + \sinh^{-1}(\sqrt{\frac{\epsilon_2}{8kT\rho_2^\infty}}|\frac{\epsilon}{h\epsilon_2}\psi_1(0) + \frac{\sigma_2}{\epsilon_2}|)$$

The rest is left to solve the above algebraic equation for $\psi_1(0)$, and the other unknowns. In the attachment, matlab file starts from solving this equation and putting them into the exact solution to this model.

As shown in [2], the potential functions is given by

$$\psi_{1,2}(x) = \frac{2kT}{q} \log \left[\frac{1 + \gamma_{1,2} e^{-\kappa_{1,2} x}}{1 - \gamma_{1,2} e^{-\kappa_{1,2} x}} \right]$$

where

$$\gamma_{1,2} = \tanh(q(\psi_{1,2}(0) - \psi^{\infty})/4kT)$$

and $1/\kappa_{1,2}$ is Debye length.

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