

# Analytical Modelling Guide

## 1 Introduction

As a preliminary investigation, in order to justify the concept of spatial patterning of a lawn of cells via the transport of a redox-active molecule from an electrode surface, a model of the concentration distribution of a given species around such an electrode must be generated. At this point, transport is defined as any molecular motility due to diffusive, electrokinetic, or bulk convective effects.

## 2 Simplification of the problem

Due to the conditions of the problem, some simplifications can be made to this initial model. Due to the fact that any transport of redox-active molecules occurs within an agar matrix, bulk convection can be discounted. In addition, it can be shown that electrokinetic effects can be discounted.

### 2.1 Discounting Electrokinetic Effects

In aqueous solution, electrostatic interactions of any type are screened due to the presence of ions in the solution. This can be imagined as follows: suppose that one inserts a positively charged plate into an aqueous solution. Anions in the solution will be attracted to the surface of this plate, and their electric fields will superpose with the electric field of the charged plate. This has the effect of cancelling out the electric field of the plate to a greater and greater extent as the distance from the plate increases. In order to quantitatively determine the effect of these attracted ions, we must use their concentration distribution, which is given by the Boltzmann equation.

$$n(z) = n_0 \exp\left(\frac{-ze\psi(x)}{k_B T}\right) \quad (1)$$

Where  $n_0$  is the mean density, or concentration, of ions,  $ze$  is the charge of the ions, and  $\psi(x)$  is the potential as a function of distance from the charged plate.

The potential  $\psi(x)$  is determined by the charge distribution of the ions in the following way:

$$\rho(z) = -\epsilon\epsilon_0 \left(\frac{d^2\psi}{dx^2}\right) \quad (2)$$

In the case where  $\rho = ze$ , or where the only ions present are those needed to balance the charge on the plate, (1) and (2) are combined to give the Poisson-Boltzmann equation.

$$\frac{d^2\psi}{dx^2} = -\left(\frac{zen_0}{\epsilon\epsilon_0}\right)\exp\left(\frac{-ze\psi(x)}{k_B T}\right) \quad (3)$$

Considering the case of a solution of a monovalent salt, such as NaCl, the Poisson-Boltzmann equation is given as follows.

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= -\left(\frac{zen_0}{\epsilon\epsilon_0}\right)\exp\left(\frac{-ze\psi(x)}{k_B T}\right) + \left(\frac{zen_0}{\epsilon\epsilon_0}\right)\exp\left(\frac{ze\psi(x)}{k_B T}\right) \\ &= \left(\frac{2zen_0}{\epsilon\epsilon_0}\right)\sinh\left(\frac{ze\psi}{k_B T}\right) \quad z = 1 \end{aligned} \quad (4)$$

For the case of a charged plate in solution, the boundary conditions are  $\lim_{x \rightarrow \infty} \psi(x) = 0$  and  $\lim_{x \rightarrow \infty} d\psi(x)/dx = 0$ . For small  $\psi$ , the approximation  $\sinh\left(\frac{ze\psi}{k_B T}\right) \approx (ze\psi/K_B T)$  (the Debye-Huckel approximation) can be used, giving the solution to (4) as

$$\psi(x) = \psi_0 \exp(-kx), \quad k = \left(\frac{2e^2 n_0 z^2}{\epsilon\epsilon_0 k_B T}\right)^{\frac{1}{2}} \quad (5)$$

Thus it can be seen that ions in an electrolyte screen the electric field in an exponential manner, the lengthscale of which is given by the Debye length,  $k^{-1}$ . It is convenient for this application to use  $mol/m^3$  to calculate the Debye length, and since the bulk electrolyte is monovalent NaCl, the equation for the Debye length becomes

$$\lambda_D = \left(\frac{\epsilon\epsilon_0 k_B T}{2e^2 N_A I}\right)^{\frac{1}{2}} \quad (6)$$

With  $N_A$  being the Avogadro number and  $I$  the ionic strength of the solution, which is equivalent to the concentration of ions in  $mol/m^3$  for monovalent salts. A NaCl concentration of  $171 mol/m^3$ , as is the NaCl concentration in LB broth, and hence in this problem, gives  $\lambda_D = 0.758 nm$ . Hence, the electric field does not penetrate any meaningful distance into the solution, and conclude that the effect of the applied field upon the transport of redox-active molecules is insignificant.

### 3 Steady State Concentration Distribution

In order to determine the steady state concentration distribution of a given species around an electrode, the problem is formulated as follows. This solution comprises a complete manual resolution of a problem in electrochemical sensing. (Bell, Seelanan and O'Hare, 2017)

1. The agar is defined as a 3 dimensional half-space, with its upper limit being the plane  $z = 0$ , and extending arbitrarily far in the radial and the  $-z$  directions.
2. The electrode on the agar plate is defined as a disk of radius  $a$ , centred on the origin, in the plane  $z = 0$ .
3. There is a constant flux  $Q$  of the species of interest through the surface of the electrode, and a no-flux condition everywhere else on the plane  $z = 0$ .
4. The problem is constructed in the form of a 2D radially symmetric (axisymmetric) diffusion problem, using cylindrical coordinates.

The governing equation for the system is taken as the diffusion equation at steady state, which is equivalent to the Laplacian of the concentration, given below in cylindrical coordinates. This also accounts for conservation of the species.

$$\begin{aligned} \nabla^2 C(r, z) &= 0 \\ \frac{\partial^2 C(r, z)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r, z)}{\partial r} + \frac{\partial^2 C(r, z)}{\partial z^2} &= 0 \end{aligned} \quad (7)$$

The boundary conditions for the problem can be written as follows.

$$\begin{aligned} D \frac{\partial C(r < a, 0)}{\partial z} &= -Q \\ D \frac{\partial C(r > a, 0)}{\partial z} &= 0 \\ \lim_{|r|, |z| \rightarrow \infty} C(r, z) &= 0 \end{aligned} \quad (8)$$

It is then helpful to rewrite the problem in a non-dimensional form, using the scalings

$$r = a\hat{r} \quad z = a\hat{z} \quad C = \frac{Qa}{D}\hat{C} \quad (9)$$

which gives the nondimensional equation

$$\frac{\partial^2 C(r, z)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r, z)}{\partial r} + \frac{\partial^2 C(r, z)}{\partial z^2} = 0 \quad (10)$$

with boundary conditions

$$\begin{aligned} \frac{\partial C(r < 1, 0)}{\partial z} &= -1 \\ \frac{\partial C(r > 1, 0)}{\partial z} &= 0 \\ \lim_{|r|, |z| \rightarrow \infty} C(r, z) &= 0 \end{aligned} \quad (11)$$

In order to solve this, the Hankel transform must be utilised. The Hankel transform is also known as the Fourier-Bessel transform, and is the 2D Fourier transform with a radially symmetric integral kernel. It is self-inverting (its inverse transform is the Hankel transform, given  $\nu > -\frac{1}{2}$ ), and is given by

$$H_\nu(\alpha) = \int_0^\infty r J_\nu(\alpha r) f(r) dr \quad (12)$$

### 3.1 Properties of the Hankel Transform

For the purposes of this problem, it is important to derive one particular property of the Hankel transform. We define a differential operator

$$A_\nu(f(r)) = -\frac{\partial^2 f(r)}{\partial r^2} - \frac{1}{r} \frac{\partial f(r)}{\partial r} + \frac{\nu^2 f(r)}{r^2} \quad (13)$$

The Hankel transform behaves such that

$$H_\nu(A_\nu(f))(\zeta) = |\zeta|^2 H_\nu(f)(\zeta) \quad (14)$$

This property is widely known and will not be proven here for the sake of simplicity.

### 3.2 Derivation of the Steady State Solution

To begin, (10) is rearranged to the form

$$\frac{\partial^2 C(r, z)}{\partial z^2} = -\frac{\partial^2 C(r, z)}{\partial r^2} - \frac{1}{r} \frac{\partial C(r, z)}{\partial r} \quad (15)$$

Using (13), it can be seen that this is equivalent to

$$\frac{\partial^2 C(r, z)}{\partial z^2} = A_0(C(r, z)) \quad (16)$$

Then, taking the Hankel transform of both sides gives

$$\frac{\partial^2 \bar{C}_0(\alpha, z)}{\partial z^2} = \alpha^2 \bar{C}_0(\alpha, z) \quad (17)$$

$$\bar{C}_0(\alpha, z) = A \exp(\alpha z) + B \exp(-\alpha z) \quad (18)$$

Using boundary conditions (11), it is obvious that  $A = 0$ . In order to find  $B$ , the derivative of the Hankel transform of  $C(r, z)$  is taken, and equated to the Hankel transform of the derivative of  $C(r, z)$ . Again, boundary conditions are used to determine  $B$ .

$$\frac{d\bar{C}_0(\alpha, z)}{dz} = -B\alpha \exp(-\alpha z) = \int_0^\infty r J_0(\alpha r) \frac{\partial C(r, z)}{\partial z} dr \quad (19)$$

$$\begin{aligned}
\frac{d\bar{C}_0(\alpha, 0)}{dz} &= -B\alpha = \int_0^\infty rJ_0(\alpha r) \frac{\partial C(r, 0)}{\partial z} dr \\
&= -\int_0^1 rJ_0(\alpha r) dr + 0 \int_1^\infty rJ_0(\alpha r) dr \\
&= \frac{J_1(\alpha)}{\alpha} \\
B &= -\frac{J_1(\alpha)}{\alpha^2}
\end{aligned} \tag{20}$$

$$\bar{C}_0(\alpha, z) = -\frac{J_1(\alpha)}{\alpha^2} \exp(-\alpha z) \tag{21}$$

From this, the concentration distribution of the species can be found by taking the inverse Hankel transform, resulting in an integral that, although difficult to evaluate analytically, can be easily computed for any desired point using a numerical integrator.

$$\begin{aligned}
C(r, z) &= \int_0^\infty \alpha J_0(\alpha r) \frac{J_1(\alpha)}{\alpha^2} d\alpha \\
&= \int_0^\infty J_0(\alpha r) J_1(\alpha) \frac{d\alpha}{\alpha}
\end{aligned} \tag{22}$$

#### Reference

Bell, C., Seelanan, P. and O'Hare, D. (2017). Microelectrode generator–collector systems for electrolytic titration: theoretical and practical considerations. *The Analyst*, 142(21), pp.4048-4057.