TMA4195 Mathematical modelling 2004

Exercise set 4

Advice and suggestions: 2004–09–14

Exercise 1: (Exam December 1990, slightly modified) We shall consider a chemical reaction involving an enzyme and a substrate. A molecule of the substrate can combine with an enzyme molecule to form a complex, which is then either broken down into the original molecules or one enzyme molecule and an end product. Schematically we can view the reaction as follows:

$$s^* + e^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} c^* \overset{k_2}{\to} e^* + p^*.$$

Here s^*, e^*, c^*,and p^* are the concentrations of substrate, enzyme, complex, and end product respectively. If these concentrations are independent of position in space and the equations are scaled by

$$s^* = \overline{s}s, \quad c^* = \overline{e}c, \quad t^* = \frac{t}{k_1\overline{e}}$$

the kinetics of the system can be written

$$\dot{s} = -s + (s + \kappa - \lambda)c, \quad \mu\dot{c} = s - (s + \kappa)c$$

where

$$\mu = \frac{\overline{e}}{\overline{s}}, \quad \kappa = \frac{k_{-1} + k_2}{k_1\overline{s}}, \quad \lambda = \frac{k_2}{k_1\overline{s}}.$$

(This is the scaling used by Lin & Segel in their book, not the later improved scaling by Segel & Slemrod.)

We shall assume that the enzyme, rather than being dissolved in water, is bound in spherical particles ("pellets") of radius a, while the substrate is made available by being dissolved in water filling the void between these pellets. The concentration of substrate in the water is kept at a constant value $\overline{s}$ (by new substrate being added as the reaction proceeds), while the enzyme concentration within each pellet has the value $\overline{e}$ when no substrate is present.

The substrate enters the pellets through diffusion with a diffusivity of D^*, so that the flux density of substrate is $-D^*\nabla s^*$. The end product is also transported by diffusion, while enzyme and complex are assumed immobile.

We shall combine the chemical kinetics described above with diffusion within one of the pellets. Use the scaling $\mathbf{x}^* = a\mathbf{x}$ for the position vector, so that the pellet is given by $|\mathbf{x}| = 1$.

(a) Give arguments supporting the equations

$$\frac{\partial s}{\partial t} = D\Delta s - s + (s + \kappa - \lambda)c, \quad \mu\frac{\partial c}{\partial t} = s - (s + \kappa)c$$

for $|\mathbf{x}| < 1$, and express D in terms of D^* and the other parameters of the problem. Here, Δ is the Laplace operator. Also justify the boundary condition $s = 1$ for $|\mathbf{x}| = 1$.

(b) After a while we assume the process is stabilized, so that the various concentrations are stationary within the pellet. Deduce an ordinary differential equation, with boundary conditions, for the determination of s as a function of $r = |\mathbf{x}|$.
Hint: If $u(\mathbf{x})$ is a radially symmetric function of $\mathbf{x}$ in three dimensional space, i.e., $u(\mathbf{x}) = v(r)$ where $r = |\mathbf{x}|$, then

$$\Delta u = \frac{1}{r^2}(r^2 v')'$$

where $'$ is differentiation with respect to r.
The total reaction rate within the pellet is the amount of substrate transformed into the end product per time unit. Express this rate in terms of $s'(1)$.

(c) Assume that $\varepsilon = \lambda/D$ is a small parameter, and find $s(r)$ to an accuracy of order ε^2. In other words, we accept an error $\mathcal{O}(\varepsilon^3)$ in the answer. (*Hint*: First solve the problem for $\varepsilon = 0$, then substitute the solution s_0 in $s = s_0 + \varepsilon s_1 + \varepsilon^2 s_2 + \cdots$ before you try to establish equations for s_1 and s_2. You may need a couple of terms from the power series $1/(a + \varepsilon b) = \sum_{k=0}^{\infty}(-1)^k(\varepsilon b)^k/a^{k+1}$ or some similar series).

(d) Assume instead that $\eta = D/\lambda$ is small. The solution $s(r)$ will now exhibit a boundary layer at $r = 1$. Solve the problem to an accuracy corresponding to an error $\mathcal{O}(\eta)$. (*Hint*: For the inner solution, let $r = 1 - \delta\rho$ where δ is a small parameter. Pick a suitable δ in relation to η. It is enough to find an approximate expression for ρ as a function of s (expressed as a definite integral)).