Problem 1 – Conduction/Convection (Beers' text 6.B.1)
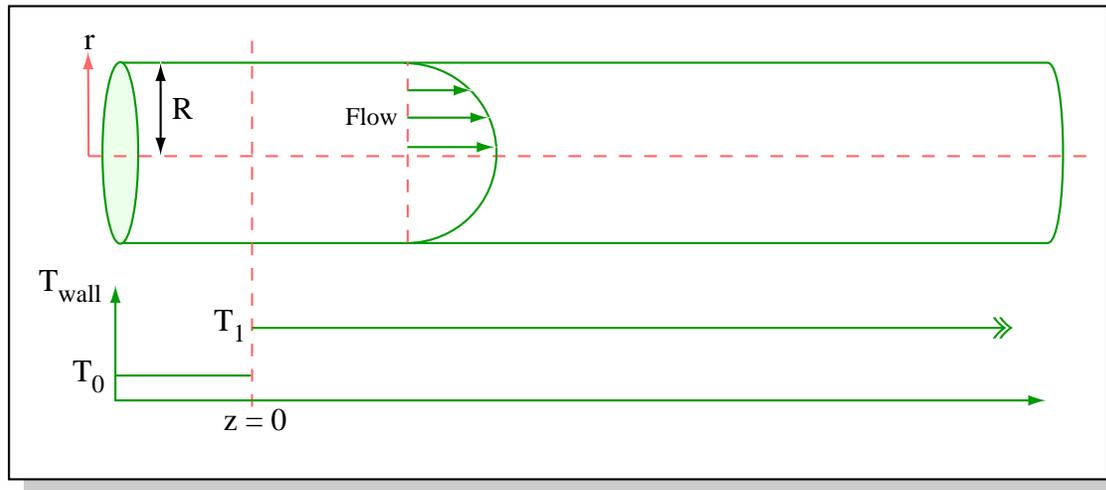

Figure by MIT OCW.

This problems involves heat conduction in a flowing Newtonian fluid with a know velocity profile (incompressible flow in a tube). The governing equation for the system is the conduction equation with convection in the z-direction:

$$\underline{v} \cdot \underline{\nabla}(\rho C_P T) = \lambda \nabla^2 T \qquad \Rightarrow \qquad v_z \frac{\partial T}{\partial z} = \frac{\lambda}{\rho C_P}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2}\right)$$

$$2U\left(1 - \left(\frac{r}{R}\right)^2\right) \cdot \frac{\partial T}{\partial z} = \frac{\lambda}{\rho C_P}\left(\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial z^2}\right)$$

In this case, U is the average velocity of fluid and can be calculated from the given Reynolds number and fluid properties. The boundary conditions for this problem were given in the radial part of the problem, but were somewhat ambiguous in the z-direction. In the z-direction, a valid boundary condition for upstream would be that $T = T_0$ at some distance upstream of the temperature change at the wall. A BC for downstream could be that the gradient (dT/dz) far downstream is zero, or that $T = T_1$ far downstream. The zero derivative boundary condition is probably better since it will be less likely to skew a solution where you do not go far enough in the z-direction. The boundary conditions used in the problem were:

$$T(r, z = -2R \cdot Pe) = T_0 \qquad\qquad T(r, z = 10R \cdot Pe) = T_1$$

$$T(r = R, z) = \begin{cases} T_0 & z < 0 \\ T_1 & z \geq 0 \end{cases} \qquad \frac{\partial T}{\partial r}(r = 0, z) = 0$$

The boundary conditions in z are equivalent to starting 2 characteristic conduction times upstream and going to 10 downstream of the temperature jump.

It is often useful to make problem non-dimensional before solving in order to formulate the problem in terms of as few parameters as possible. For this problem, we choose the following non-dimensional variables:

$$\eta \equiv \frac{r}{R} \qquad \xi \equiv \frac{z}{R \cdot Pe} \qquad \theta \equiv \frac{T - T_0}{T_W - T_0} \qquad where: \quad Pe = \frac{2UR}{\alpha} \quad and \quad \alpha = \frac{\lambda}{\rho C_P}$$

Carefully applying these non-dimensional variables, one will find the following equation:

$$\frac{\partial\theta}{\partial\eta}+\eta\frac{\partial^2\theta}{\partial\eta^2}+\frac{\eta}{Pe^2}\frac{\partial^2\theta}{\partial\xi^2}-\eta\left(1-\eta^2\right)\cdot\frac{\partial\theta}{\partial\xi}=0$$

$$\theta\left(\eta,\xi=-2\right)=0 \qquad\qquad \theta\left(\eta,\xi=10\right)=1$$

$$\theta\left(\eta=1,\xi\right)=\begin{cases}0 & \xi<0 \\ 1 & \xi\geq0\end{cases} \qquad\qquad \frac{\partial\theta}{\partial\eta}\left(\eta=0,\xi\right)=0$$

You can see that the non-dimensional form is much simpler, and the boundary conditions are extremely simple, which is a nice aspect since the units in many problems can be tedious. We also multiply through by the radius term to avoid any potential problems at r = 0.
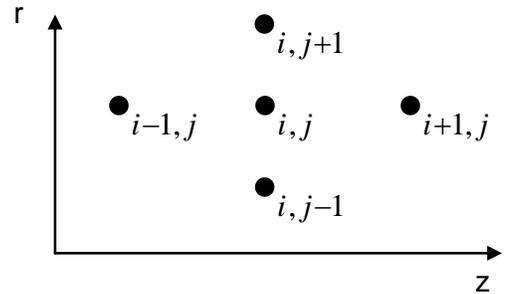
Now we need to work on the discretization, keeping in mind that in problems with convection, upwind differencing is usually the preferred method to ensure stability. Therefore, we will use upwind difference in the z-direction for first derivatives, central difference in the radial direction for first derivatives, and central difference for the 2nd derivatives in both directions.

We need to take the 2-D grid of points and translate it into a 1-D vector of state variables for the entire physical space. This can be accomplished by the following equation:

$$n\left(i,j\right)=\left(i-1\right)N_{radial}+j$$

This formula takes the vector for each radial cross-section and stacks them on top of each other. The discretizations are written as:

$$\left.\frac{\partial\theta}{\partial\xi}\right|_{\xi_i}=\frac{\theta_{i,j}-\theta_{i-1,j}}{\Delta\xi} \qquad \left.\frac{\partial^2\theta}{\partial\xi^2}\right|_{\xi_i}=\frac{\theta_{i+1,j}-2\theta_{i,j}+\theta_{i-1,j}}{\left(\Delta\xi\right)^2} \qquad \left.\frac{\partial\theta}{\partial\eta}\right|_{\eta_i}=\frac{\theta_{i,j+1}-\theta_{i,j-1}}{2\Delta\eta} \qquad \left.\frac{\partial^2\theta}{\partial\eta^2}\right|_{\eta_i}=\frac{\theta_{i,j+1}-2\theta_{i,j}+\theta_{i,j-1}}{\left(\Delta\eta\right)^2}$$

Now that we have the discretization formulae, we can rewrite the differential equation as a set of algebraic equations. The internal points of the grid can be described by:

$$\left(\frac{\theta_{i,j+1}-\theta_{i,j-1}}{2\Delta\eta}\right)+\eta_{i,j}\left(\frac{\theta_{i,j+1}-2\theta_{i,j}+\theta_{i,j-1}}{\left(\Delta\eta\right)^2}\right)+\frac{\eta_{i,j}}{Pe^2}\left(\frac{\theta_{i+1,j}-2\theta_{i,j}+\theta_{i-1,j}}{\left(\Delta\xi\right)^2}\right)-\eta_{i,j}\left(1-\eta_{i,j}^2\right)\left(\frac{\theta_{i,j}-\theta_{i-1,j}}{\Delta\xi}\right)=0$$

Grouping the terms for each state variable, we get the following:

$$\left(\frac{1}{2\Delta\eta}+\frac{\eta_{i,j}}{\left(\Delta\eta\right)^2}\right)\theta_{i,j+1}+\left(\frac{\eta_{i,j}}{Pe^2\left(\Delta\xi\right)^2}\right)\theta_{i+1,j}+\left(-\frac{2\eta_{i,j}}{\left(\Delta\eta\right)^2}-\frac{2\eta_{i,j}}{Pe^2\left(\Delta\xi\right)^2}-\frac{\eta_{i,j}\left(1-\eta_{i,j}^2\right)}{\Delta\xi}\right)\theta_{i,j}$$

$$+\left(\frac{\eta_{i,j}}{Pe^2\left(\Delta\xi\right)^2}+\frac{\eta_{i,j}\left(1-\eta_{i,j}^2\right)}{\Delta\xi}\right)\theta_{i-1,j}+\left(\frac{\eta_{i,j}}{\left(\Delta\eta\right)^2}-\frac{1}{2\Delta\eta}\right)\theta_{i,j-1}=0$$

$$for:\ 2\leq i\leq N_z-1 \qquad and \qquad 2\leq j\leq N_{radial}-1$$

The boundary conditions are defined as:

$$\theta_{i,j} = 0 \qquad\qquad\qquad\qquad\qquad for\ i = 1\ and\ 2 \le j \le N_{radial} - 1$$

$$\theta_{i,j} = 1 \qquad\qquad\qquad\qquad\qquad for\ i = N_z\ and\ 2 \le j \le N_{radial} - 1$$

$$\theta_{i,j} = \begin{cases} 0 & \xi_{i=1} + (i-1)\Delta\xi < 0 \\ 1 & \xi_{i=1} + (i-1)\Delta\xi \ge 0 \end{cases} \qquad for\ j = N_{radial}$$

$$\theta_{i,j} - \frac{4}{3}\theta_{i,j+1} + \frac{1}{3}\theta_{i,j+2} = 0 \qquad\qquad for\ j = 1$$

We now have equations for all points in the grid, including the boundary conditions. The BC's will also require the b-vector (in A*x = b) to be specified at a few points in *i, j* space (with all other elements being zero). The translation formula from earlier can be used to make a sparse matrix filled with the coefficients of the state variables. For the internal points, the equations are:

$$A\left(n_{i,j}, n_{i,j}\right) = -\frac{2\eta_{i,j}}{(\Delta\eta)^2} - \frac{2\eta_{i,j}}{Pe^2(\Delta\xi)^2} - \frac{\eta_{i,j}\left(1 - \eta_{i,j}^2\right)}{\Delta\xi}$$

$$A\left(n_{i,j}, n_{i+1,j}\right) = \frac{\eta_{i,j}}{Pe^2(\Delta\xi)^2} \qquad\qquad A\left(n_{i,j}, n_{i,j+1}\right) = \frac{1}{2\Delta\eta} + \frac{\eta_{i,j}}{(\Delta\eta)^2}$$

$$A\left(n_{i,j}, n_{i-1,j}\right) = \frac{\eta_{i,j}}{Pe^2(\Delta\xi)^2} + \frac{\eta_{i,j}\left(1 - \eta_{i,j}^2\right)}{\Delta\xi} \qquad\qquad A\left(n_{i,j}, n_{i,j-1}\right) = \frac{\eta_{i,j}}{(\Delta\eta)^2} - \frac{1}{2\Delta\eta}$$

Similar equations can be written for the boundary conditions that relate the state variables. Note the all of the coefficients for a given equation occur on the same row of the A-matrix. The A-matrix is multiplied by the state variable vector to yield the equations at each point in physical space. The system of linear equations that needs to be solved is: $\underline{\underline{A}} \cdot \underline{\theta} = \underline{b}$.

Figures:
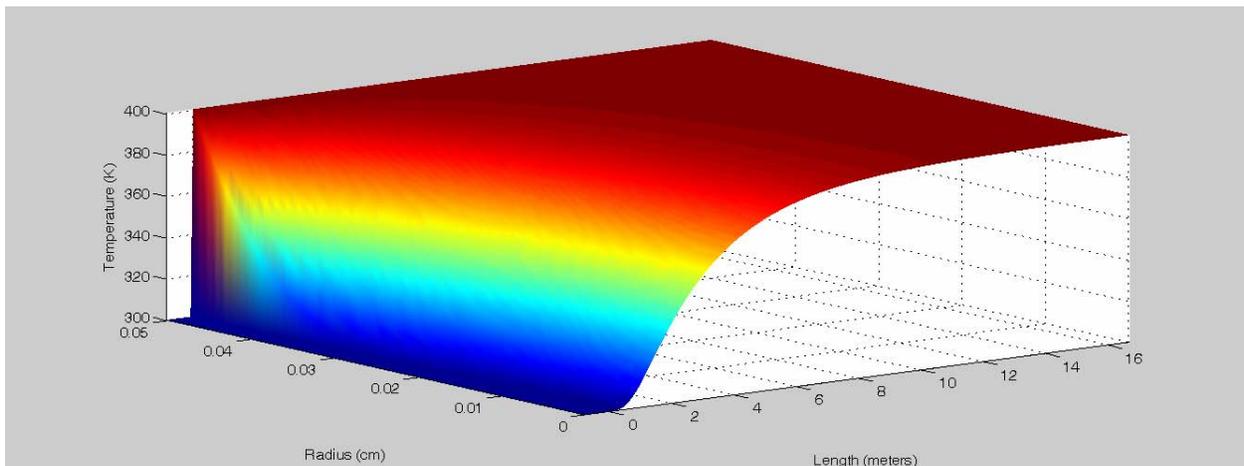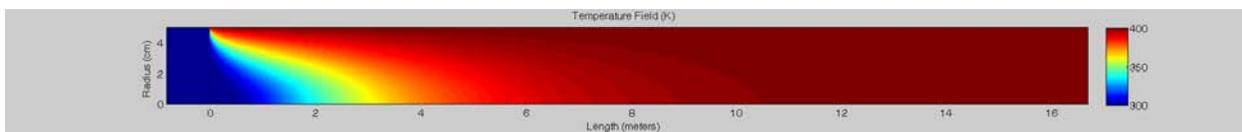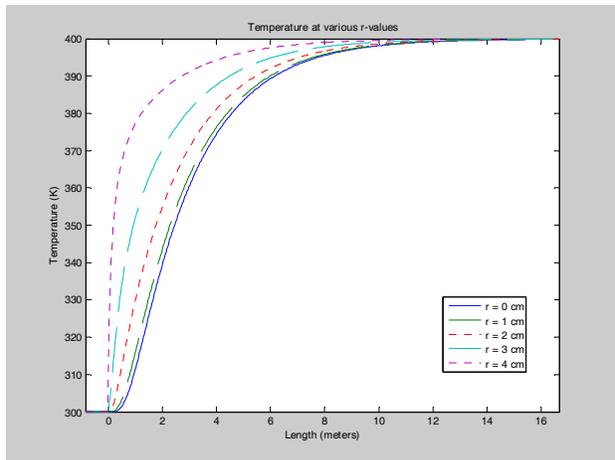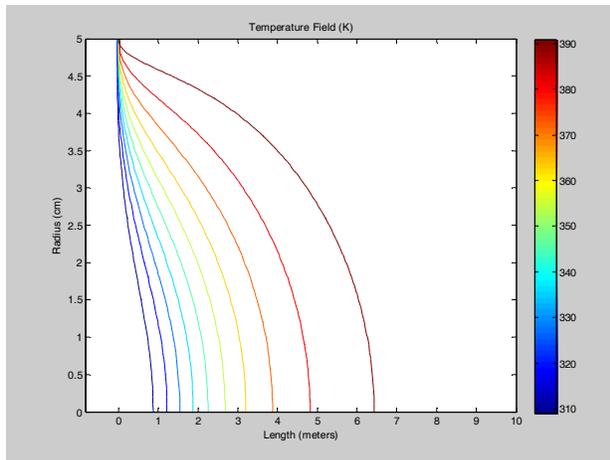
You can also look at the sparsity pattern of the system matrix using the "spy" command. This just shows the top left corner. You can see the tri-diagonal with two diagonals offset from the center by the number of points in the radial direction. The gaps correspond to rows that specify the boundary conditions.
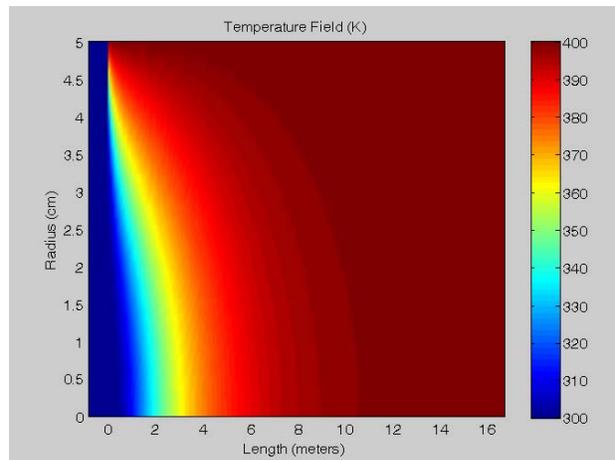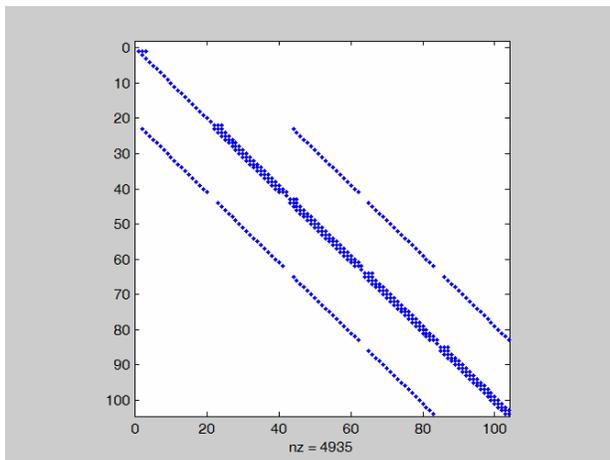
Problem 2: Reaction and Diffusion in a Spherical Catalyst Bead (Beers' text 6.B.1)

In the problem, we are concerned with a spherical catalyst particle with diffusion, and a given external mass transfer situation (Sherwood number). The general equation for this situation is:

$$\frac{\partial S}{\partial t} = 0 = D_{S,gel} \nabla^2 S + R_V \qquad \Rightarrow \qquad 0 = D_{S,gel} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dS}{dr} \right) \right) - \frac{\rho_E V_m S}{K_m + S}$$

One must be careful when dealing with the units in this problem, and converting everything to moles-m^3-sec-kg may be advisable. We can expand the spherical derivatives to get:

$$0 = r \frac{d^2 S}{dr^2} + 2 \frac{dS}{dr} - \frac{r \rho_E}{D_{S,gel}} \frac{V_m S}{K_m + S}$$

The boundary conditions for this problem are symmetry at r = 0, and that the fluxes are equal at r = R. These essentially result in:

$$\frac{dS}{dr}(r = 0) = 0 \qquad\qquad D_{S,gel} \frac{dS}{dr}(r = R) = k_{mass} \left(S_{bulk} - S_{surface} \right)$$

We can do a discretization based on uniform spacing in the radial direction:

$$0 = r_i \left(\frac{S_{i+1} - 2S_i + S_{i-1}}{\Delta r^2} \right) + 2 \left(\frac{S_{i+1} - S_{i-1}}{2\Delta r} \right) - \frac{r_i \rho_E}{D_{S,gel}} \frac{V_m S_i}{K_m + S_i}$$

$$S_i - \frac{4}{3} S_{i+1} + \frac{1}{3} S_{i+2} = 0 \quad @ \ i \ \ for \ r = 0$$

$$\frac{S_i - S_{i-1}}{\Delta r} = \frac{k_{mass}}{D_{S,gel}} \left(S_{bulk} - S_i \right) \quad @ \ i \ \ for \ r = R$$

One thing to note is that boundary condition at R can behave differently depending on how it is written, due to numerical issues. It is more robust if written as above. I found that if it is written with the D and k_{mass} on different sides, then you must multiple the residual by 1e6 or 1e9 in order to force tight convergence at this point.

Plot the concentration profiles (using a scaled radius):

Close-up of small radii
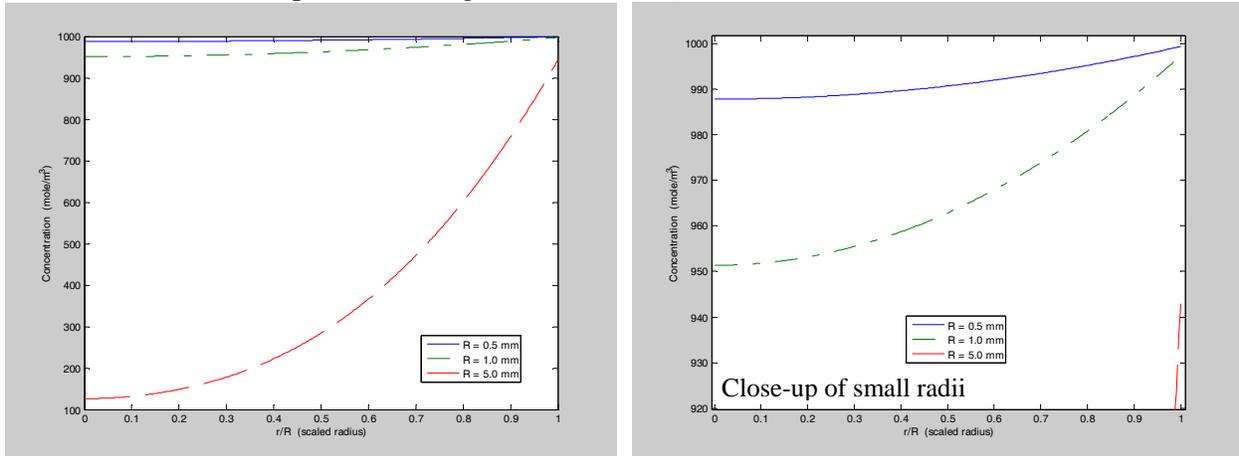
Consumption Rates:

```
Results for R = 0.0005 meters:
[S] at the bead surface:  999.3425 moles/m^3
Consumption Rate:  1.4458e-011 moles/sec
Consumption Rate per kg of Enzyme:  2.7614 moles/sec S per kg E

Results for R = 0.001 meters:
[S] at the bead surface:  997.3773 moles/m^3
Consumption Rate:  1.1535e-010 moles/sec
Consumption Rate per kg of Enzyme:  2.7538 moles/sec S per kg E

Results for R = 0.005 meters:
[S] at the bead surface:  943.5237 moles/m^3
Consumption Rate:  1.2419e-008 moles/sec
Consumption Rate per kg of Enzyme:  2.372 moles/sec S per kg E
```

Based on these consumption rates, one would want to chose the bead size of 0.5 mm, since its results in the highest consumption rate per mass of enzyme.

Another point of interest may be the concentration of S at the particle surface, which are shown.

One problem that I found was getting the boundary conditions to be satisfied well, particularly at the surface of the bead. One would expect the flux calculated from the inside ($D*dS/dr$) would equal the flux from the outside ($k*(S_{bulk}-S_{surface})$), but this was not always the case. The boundary conditions are something that you definitely know and want to force to be true to high accuracy. This may require that you weight the BC equations by multiplying them by something like 1e6 or 1e9. This will force these to be satisfied very accurately, as should force the equal flux condition to be true.

Homework 8

November 1, 2006

Problem3

Velocity Profile

Since the diffusion of A into the solvent film does not effect the density ρ and viscosity μ of the liquid, we can calculate the velocity profile independently of the concentration of A, B or AB in the solvent. The navier stokes equation for velocity v_z that is changing only in y direction is as follows.

$$\rho g_z + \mu \left[\frac{\partial^2 v_z}{\partial y^2} \right] = 0 \tag{1}$$

The velocity is 0 at $y = b$ and the derivative of velocity is 0 at the $y = 0$, which gives us our 2 boundary conditions. To obtain the second boundary condition we have assumed that the viscosity of air is 0. Solving the above equation analytically we get

$$v_z = -\frac{\rho g_z}{2\mu}(y^2 - b^2) = 85.09(y^2 - b^2) \text{ cm/s} \tag{2}$$

The mass balance equations for any species i is

$$v_z \frac{\partial C_i}{\partial z} = D_i \left[\frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right] + R(C_A, C_B, C_{AB}) \tag{3}$$

The boundary conditions of this problem in the y-direction is given by Equation 4. The boundary condtions for B and C implies that they don't diffuse out of the liquid film.

$$C_{A(y=0)} = H_A p_A \quad \left. \frac{\partial C_A}{\partial y} \right|_{(y=b)} = 0$$

$$\left. \frac{\partial C_B}{\partial y} \right|_{(y=0)} = 0 \quad \left. \frac{\partial C_B}{\partial y} \right|_{(y=b)} = 0$$

1

$$\frac{\partial C_C}{\partial y}\bigg|_{(y=0)} = 0 \quad \frac{\partial C_C}{\partial y}\bigg|_{(y=b)} = 0 \qquad (4)$$

The boundary conditions of this problem in the z-direction is given by Equation 5. The boundary conditions at $z = L$ is not rigorously true, but is a first guess approximation.

$$C_{A(z=0)} = 0 \quad \frac{\partial C_A}{\partial z}\bigg|_{(z=L)} = 0$$

$$C_{B(z=0)} = C_{B0} \quad \frac{\partial C_B}{\partial z}\bigg|_{(z=L)} = 0$$

$$C_{C(z=0)} = 0 \quad \frac{\partial C_C}{\partial z}\bigg|_{(z=L)} = 0 \qquad (5)$$

Scaling Analysis

Let us scale the problem such that $Z = z/L$ and $Y = y/b$. Doing so the differential equation gets transformed to

$$v_z \frac{\partial C_i}{L \partial Z} = D_i \left[\frac{\partial^2 C_i}{b^2 \partial Y^2} + \frac{\partial^2 C_i}{L^2 \partial Z^2} \right] + R(C_A, C_B, C_{AB}) \qquad (6)$$

$$\frac{\partial C_i}{\partial Z} = \left(\frac{D_i L}{v_z b^2} \right) \frac{\partial^2 C_i}{\partial Y^2} + \left(\frac{D_i}{v_z L} \right) \frac{\partial^2 C_i}{\partial Z^2} + \left(\frac{L}{v_z} \right) R(C_A, C_B, C_{AB}) \qquad (7)$$

We can evaluate the approximate values of all the constant multipying factors in front of the different terms to get an approximate importance of each of these terms and the length scale that they are valid at. In our analysis the reference term is $\frac{\partial C_i}{\partial Z}$ with which all the other terms are compared.

- $\frac{\partial^2 C_i}{\partial Y^2}$

  Lets look at the coefficient of $\frac{\partial^2 C_i}{\partial Y^2}$.

  $$\frac{D_i L}{v_z b^2} = \frac{10^{-5} \times 50}{85 \times 0.1^2} \approx 10^{-3}$$

  The dimensionless length scale over which $\frac{\partial^2 C_i}{\partial Y^2}$ term becomes comparable to term $\frac{\partial C_i}{\partial Z}$ can be estimated as shown below.

  $$\frac{\delta C_i}{\delta Z} \approx 10^{-3} \frac{\delta C_i}{\delta Y^2}$$

  $$\delta Y^2 \approx 10^{-3} \delta Z$$

Thus if we divide the dimensionless length scale Z into 10 subdivisions i.e. $\delta Z = 0.1$, then dimensionless Y has to be divided into 100 parts. Thus for our case, the length scale of Y that is important is 0.01 ($y \approx 0.001$ cm). This analysis tells us that in y direction in absence of reaction the length scale that we have to use is of the order 0.001. Such fine meshing will result in a number of grid points 100 in the y direction and 10 in the z direction. Each species has concentration at each grid point and thus there are 3 variables per grid point. Thus this will result in a system of 3000 equations in as many variables and the Jacobian of the system will have an the order of 10^7 entries. This is a huge number and will almost surely result in matlab complaining about running out of memory, and if not that then the cpu time will be very large. This brings us to the requirement to do adaptive meshing. Later in the solution we will look at how to do adaptive meshing, so that we can capture the variations of concentration in the narrow region close to y=0.

- $\frac{\partial^2 C_i}{\partial Z^2}$

  The coefficient of this term is

  $$\frac{D_i}{v_z L} = \frac{10^{-5}}{85 \times 50} \approx 10^{-9}$$

  The length scale over which $\frac{\partial^2 C_i}{\partial Z^2}$ term becomes comparable to term $\frac{\partial C_i}{\partial Z}$ can be estimated as

  $$\frac{\delta C_i}{\delta Z} \approx 10^{-9} \frac{\delta C_i}{\delta Z^2}$$

  $$\delta Z \approx 10^{-9}$$

  The above analysis tell us that for our geometry the diffusion term in the z-direction will be significant if we chose our δZ close to 10^{-9}. Thus for all practical purposes we can chose to ignore this term, although including it would not make any difference.

- Reaction Term

  The importance of the reaction term can be judged by evaluating the coefficient in front of it

  $$\frac{kLC_{B0}}{v_z} = \frac{10^{-2} \times 50 \times 1}{85} \approx 10^{-2}$$

3

The length scale in the Z direction over which the reaction effects the concentration of A is

$$\frac{\delta C_A}{\delta Z} \approx 10^{-2} C_A$$

$$\delta Z \approx 10^2$$

Thus in our problem we dont expect the reaction rate to play a very important role. If the length of the channel was 5 m instead of 50 cm, then perhaps the reaction will enhance the absorption of A into the liquid channel.

Nonuniform Grid

To see the change in concentration of A in the z direction we divide the z axis into 2 regions, first region goes from 0 to 0.01 cm and the next region goes from 0.01 cm to 0.1 cm. In the first region we put 20 uniformly placed grid points and in the second region we put another 10 uniformly placed grid points. The presence of non-uniform grid points requires us to calculate new discretization formulas. To do this we look at any three points in a row with coordinates x_1, x_2 and x_3, with the function value of f_1, f_2 and f_3. We can estimate the function which passes through these points using a second order lagrange polynomial (Beer's book pg-226). The polynomial is given as

$$f(x) = f_1 \frac{(x - x_2)(x - x_3)}{(x_1 - x_2)(x_1 - x_3)} + f_2 \frac{(x - x_1)(x - x_3)}{(x_2 - x_1)(x_2 - x_3)} + f_3 \frac{(x - x_1)(x - x_2)}{(x_3 - x_1)(x_3 - x_2)}$$

To calculate the derivative and second-derivative at the central point $x = x_2$, we just take the first derivative and the second derivative of the above equation and equate $x = x_2$. Doing the same we obtain the following formulas for $f'(x = x_2)$ and $f''(x = x_2)$.

$$f'(x = x_2) = f_1 \frac{(x_2 - x_3)}{(x_1 - x_2)(x_1 - x_3)} + f_2 \frac{2x_2 - x_3 - x_1}{(x_2 - x_1)(x_2 - x_3)} + f_3 \frac{(x_2 - x_1)}{(x_3 - x_1)(x_3 - x_2)} \tag{8}$$

$$f''(x = x_2) = \frac{2f_1}{(x_1 - x_2)(x_1 - x_3)} + \frac{2f_2}{(x_2 - x_1)(x_2 - x_3)} + \frac{2f_3}{(x_3 - x_1)(x_3 - x_2)} \tag{9}$$

Equation (8) gives the central difference formulation of the first derivative and can result in numerical noise leading to oscillations. For our problem we will just use the upwind difference scheme which can be written as

$$f'(x = x_2) = \frac{(f_2 - f_1)}{(x_2 - x_1)} \tag{10}$$

Flux of A

We can calculate the flux of species A into the channel using the equation

$$F_A(z, y = 0) = -D_A \frac{\partial C_A}{\partial y}\bigg|_{z,y=0} \tag{11}$$

The average flux of A per unit area can be calculated using the formula given in Eqation 12, which is similar to using the trapezoid rule

$$F_A = \sum_i -D_A \left[\frac{\partial C_A}{\partial y}\bigg|_{z_i,y=0} + \frac{\partial C_A}{\partial y}\bigg|_{z_{i-1},y=0} \right] \frac{(z_i - z_{i-1})}{2L} \tag{12}$$

$$\frac{\partial C_A}{\partial y}\bigg|_{z_i,y=0} = \frac{-3C_A(z_i,0) + 4C_A(z_i,1) - C_A(z_i,2)}{2\Delta y} \tag{13}$$

Program Structure

The code that does all the above is given in 4 separate files

- `problem3_bvp_nonuniformgrid.m` This is the main program which initializes all the variables and calls `fsolve`.

- `solve_c_nonuniformgrid.m` This function is called by `fsolve` and it returns the residuals to `fsolve`. One could ideally make it return the jacobian as well, but i have not done it here. Making the jacobian sparse and returning it will result in faster computations.

- `velocity.m` This function returns the velocity of liquid at any given value of y.

- `reactionRate.m` Returns the rate of reaction for a given conentration of A, B and AB.

- `derivative.m` Calculates the derivative using finite difference at any given grid point. This function is useful when one is dealing with non-uniform grid spacing.

- `doublederivative.m` Calculates the second derivative finite difference at any given grid point. This function is useful when one is dealing with non-uniform grid spacing.

Result

- **Zero Reaction Rate**

  The sample input output and grphs for this run is given below.

  ```
  >> problem3_bvp_nonuiformgrid(0)
  ```

  ```
                                   Norm of  First-order Trust-region
    Iteration  Func-count      f(x)       step    optimality     radius
        0         1501       0.23                     0.1          1
        1         3002       0.059986      1         0.113         1
        2         4503    1.81919e-018  1.04378    1.86e-007      2.5
  Optimization terminated:  first-order optimality is less than
  options.TolFun.
  The total flux of A into the channel is:  4.9196e-007 mol/cm^2/s
  >>
  ```
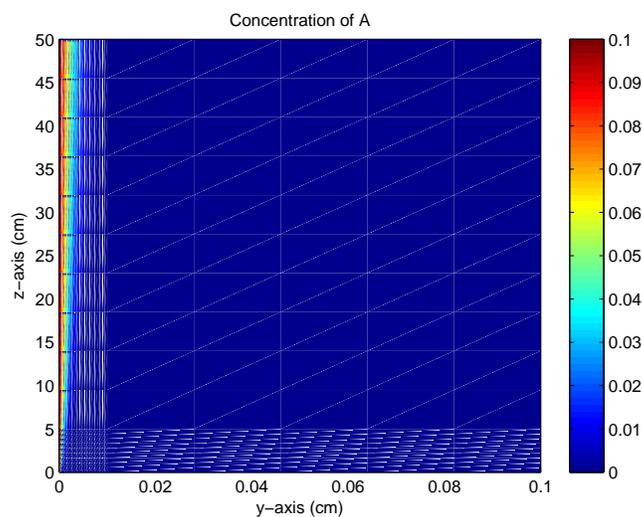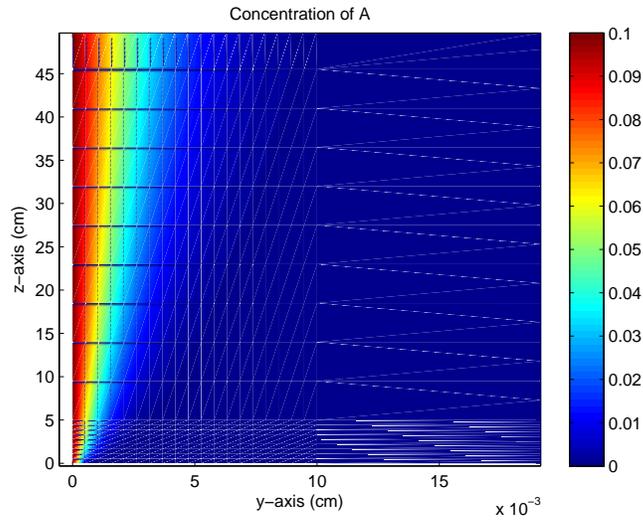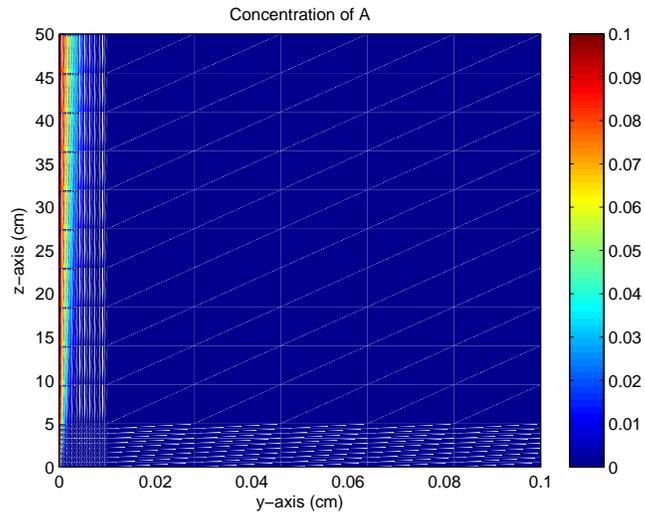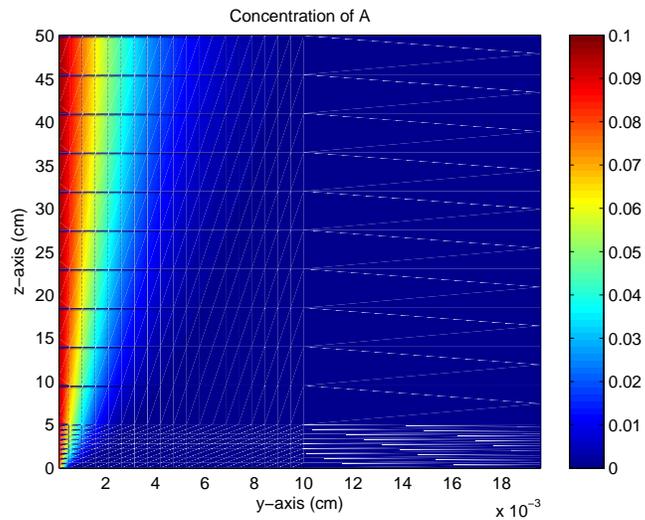

Figure 1: Concentration of A without reaction

- **Zero Reaction Rate**

  The sample input output and graphs for this run is given below.

  ```
  >> problem3_bvp_nonuiformgrid(1e-2)
  ```

Figure 2: Magnified view at the boundary

Iteration	Func-count	f(x)	Norm of step	First-order optimality	Trust-region radius
0	1501	0.231242		0.17	1
1	3002	0.060299	1	0.164	1
2	4503	4.65734e-014	1.04396	5.34e-007	2.5

```
Optimization terminated:  first-order optimality is less than
options.TolFun.
The total flux of A into the channel is:  4.928e-007 mol/cm^2/s
>>
```

Figure 3: Concentration of A with reaction

Figure 4: Magnified view at the boundary showing concentration of A
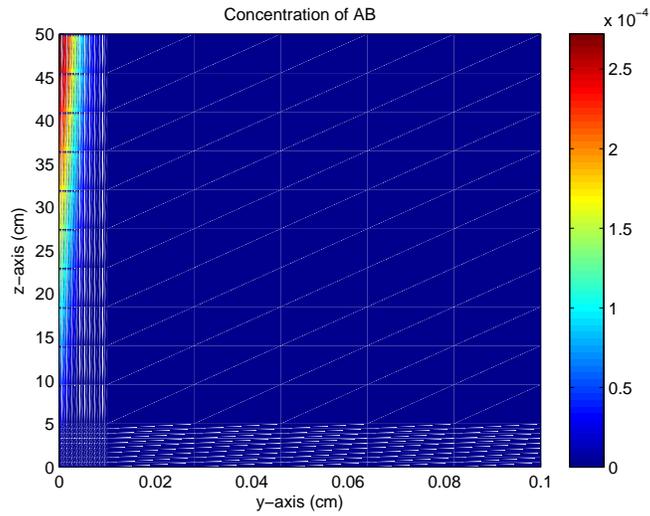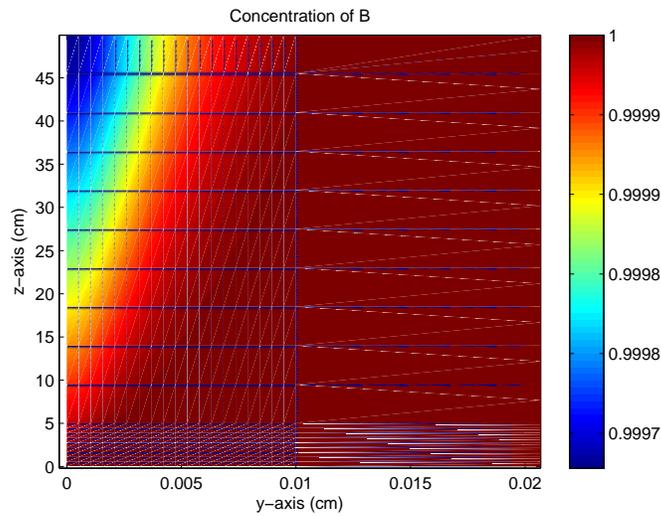
Figure 5: Concentration of B with reaction

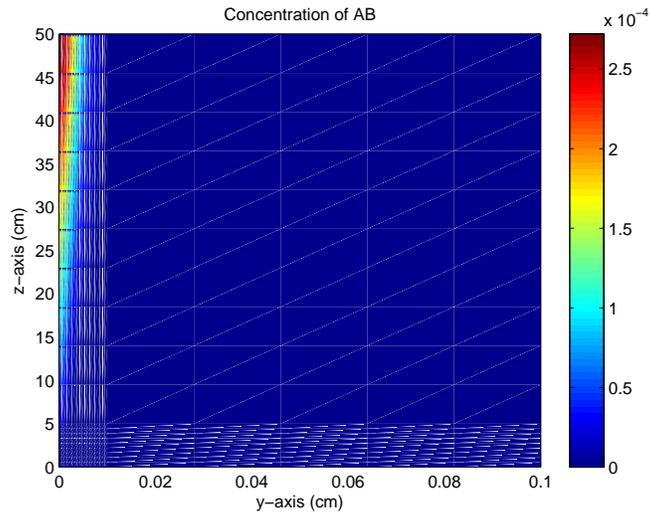Figure 6: Magnified view at the boundary showing concentration of B
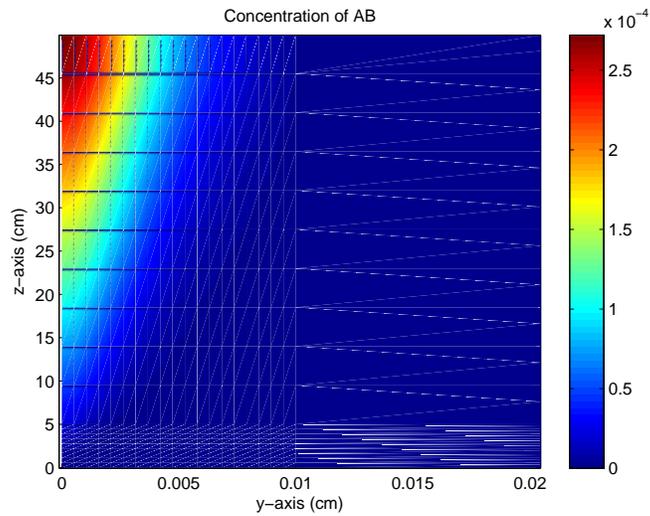
Figure 7: Concentration of AB with reaction

Figure 8: Magnified view at the boundary showing concentration of AB