A Collocation Primer on the Numerical Solution to Diffusion and Reaction in a Spherical Pellet

Steady-state reaction with diffusion problems lead to second-order ordinary differential equations for one-dimensional situations, such as a spherical pellet. Since one does not know both boundary conditions at the same location, these problems fall into the general class known as boundary value problems. In reaction/diffusion problems we specify the concentration or match the fluxes at the pellet surface for one of the boundary conditions, and specify the gradient at the pellet center for the second boundary condition. In limited cases, such as single reactions, positive order kinetics and isothermal, the reaction/diffusion problem can be solved analytically.

Unfortunately the number of reaction/diffusion problems that can be solved analytically is very limited and numerical approaches are necessary. When the pellet has symmetry and can be reduced to a one dimensional problem, such as a spherical pellet, the collocation approach outlined here will work. If the pellet were a short cylinder, finite element methods or other techniques would be required. The collocation approach could be used for multiple reactions, for complex reaction rate expressions and for non-isothermal pellets. Indeed, collocation methods were used to generate the numerical solutions presented in the text.

Let's use the analytical solution for a first-order reaction in an isothermal spherical pellet to illustrate the approach and to benchmark our solution. As illustrated in the text the differential equation and boundary conditions are

$$\frac{d^2\overline{c}}{d\overline{r}^2} + \frac{2}{\overline{r}}\frac{d\overline{c}}{d\overline{r}} - \Phi^2\overline{c} = 0 \tag{1}$$

$$\overline{c} = 1 \text{ at } \overline{r} = 3 \qquad \frac{d\overline{c}}{d\overline{r}} = 0 \text{ at } \overline{r} = 0$$

$$\overline{c}(\overline{r}) = \frac{3}{\overline{r}}\frac{\sinh \Phi\overline{r}}{\sinh 3\Phi} \tag{2}$$

Equation 2 is plotted in Figure 1 for the case where $\Phi = 5$. We see how steep this curve is, meaning it has what appears to be a value of zero and then increases to a value of unity in the outer shell of the sphere. All functions, such as Eqn 2 can be expressed as a series of orthogonal functions, such as Fourier series, Legendre polynomials, Hermite polynomials, etc. The steeper the function, the higher the order of polynomial needed to describe it. Then to describe (or fit) the function, we need to select a high enough order and find the coefficients. This is essentially what collocation does.

We approximate the function by passing a polynomial through the function at selected points.

$$c(r) = \sum_{i}^{n_c} a_i c_i(r) \tag{3}$$

where $c_i(r)$ is the i^{th} orthogonal function. In the write up, five points are selected, and they are not sufficient when $\Phi = 5$. Ten points are sufficient as will be shown below.

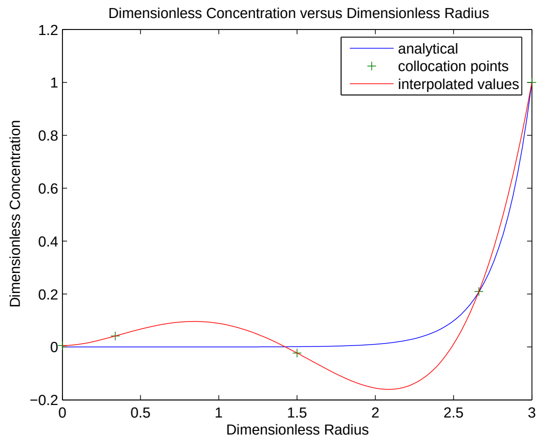

Figure 1: Numerical solution for five collocation points and the analytical solution when $\Phi = 5$.

The placement of the points is done by the program `colloc` in either Matlab, which you can find on the website, or Octave. If you run `colloc`, you will find the five points, which are indicated in Figure 1, are located at the dimensionless radial positions $\overline{r}$ (in the `colloc` program the variable is called R)

$$R = [0 \;\; 0.3381 \;\; 1.5000 \;\; 2.6619 \;\; 3.0000]$$

The derivatives of the polynomial interpolant can be computed as linear combinations of the values at the collocation points

$$\left.\frac{dc}{dr}\right|_{r_i} = \sum_{j}^{n_c} A_{ij} c_j \tag{4}$$

$$\left.\frac{d^2c}{dr^2}\right|_{r_i} = \sum_{j}^{n_c} B_{ij} c_j \tag{5}$$

For our problem, with five collocation points, there will be five values of c.

$$c = [c_1 \;\; c_2 \;\; c_3 \;\; c_4 \;\; c_5] \tag{6}$$

We now use Equations 4 and 5 to satisfy the boundary conditions and the differential equation (Equation 1) at the appropriate points. We will be writing five algebraic equations and these will be solved simultaneously to find the five values of c in Equation 6. The programs on the website set the left-hand sides of these equations equal to a variable `retval(n`$_i$`)` so it will be used here. When running the program, we force the end points to the boundaries. Then the first collocation point $n = 1$ is at $\overline{r} = R(1) = 0.0$ and here we must statisfy the boundary condition

$$\frac{d\overline{c}}{d\overline{r}} = 0$$

This can be recast using Equation 4

$$\text{retval}(1) = A_{11}c_1 + A_{12}c_2 + A_{13}c_3 + A_{14}c_4 + A_{15}c_5 \tag{7}$$

or using Matlab/Octave syntax

$$\text{retval}(1) = A(1,:) * c$$

The values of the weighting coefficients A are generated by the program `colloc` based on our instructions to force the boundaries to the end points and that there were five collocation points. For this particular case the matrix A is given by

$$A = \begin{bmatrix} A_{11} & A_{12} & A_{13} & A_{14} & A_{15} \\ A_{21} & A_{22} & A_{23} & A_{24} & A_{25} \\ A_{31} & A_{32} & A_{33} & A_{34} & A_{35} \\ A_{41} & A_{42} & A_{43} & A_{44} & A_{45} \\ A_{51} & A_{52} & A_{53} & A_{54} & A_{55} \end{bmatrix}$$

$$A = \begin{bmatrix} -4.3333 & 4.9294 & -0.88889 & 0.62612 & -0.33333 \\ -1.7746 & 1.2910 & 0.68853 & -0.43033 & 0.22540 \\ 0.50000 & -1.0758 & 0.0 & 1.0758 & -0.50000 \\ -0.22540 & 0.43033 & -0.68853 & -1.2910 & 1.7746 \\ 0.33333 & -0.62612 & 0.88889 & -4.9294 & 4.3333 \end{bmatrix}$$

Next we satify Equation 1 at any collocation point not at a boundary, *i.e.,* $\overline{r} \neq 0$ and $\overline{r} \neq 3$. The algebraic equation becomes

$$0 = \sum B_{ij}c_j + \frac{2}{r_i}\sum A_{ij}c_j - \Phi^2 c_j$$

and for collocation Point 2 ($R(2) = 0.3381$)

$$\begin{aligned} \text{retval}(2) \quad = \quad & B_{21}c_1 + B_{22}c_2 + B_{23}c_3 + B_{24}c_4 + B_{25}c_5 \\ & + \frac{2}{R_2}A_{21}c_1 + \frac{2}{R_2}A_{22}c_2 + \frac{2}{R_2}A_{23}c_3 + \frac{2}{R_2}A_{24}c_4 + \frac{2}{R_2}A_{25}c_5 \\ & - \Phi^2 c_2 \end{aligned}$$

or using Matlab/Octave syntax

$$\text{retval}(2) = B(2,:) * c + \frac{2}{R(2)} * A(2,:) * c - \Phi^2 * c(2) \tag{8}$$

As with the weights for A, there is a corresponding (5×5) B matrix of weights for the second derivative that is generated by the program `colloc`. You can work out the specific forms of the two algebraic equations at the remaining interior collocations points, Point 3 and Point 4. These are represented here using Matlab/Octave syntax.

$$\text{retval}(3) = B(3,:) * c + \frac{2}{R(3)} * A(3,:) * c - \Phi^2 * c(3) \tag{9}$$

$$\text{retval}(4) = B(4,:) * c + \frac{2}{R(4)} * A(4,:) * c - \Phi^2 * c(4) \tag{10}$$

Finally at the last collocation point, $R(5) = 3.0$, we have to satisfy the boundary condition that $\overline{c} = 1$.

$$0 = 1 - c_5 \text{ and in Matlab/Octave syntax, retval}(5) = 1 - c(5) \tag{11}$$

As an aside, we might equally well apply the boundary condition at the surface

$$\frac{d\overline{c}}{d\overline{r}} = \frac{k_m a}{D_e}(1 - \overline{c}) \text{ and in Matlab syntax, retval}(5) = A(5,:) * c - \frac{k_m a}{D_e} * (1 - c(5))$$

At this point the five concentrations in the c vector are found using the Matlab/Ocatave function `fsolve` that minimizes the `retval` vector defined with the five equations, Equations 7 to 11.

You can explore how this works using the Learning Module "First Order Pellet." Figures 1 and 2 illustrate the simulation for $\Phi = 5$, and five and ten collocation points, respectively. Notice that with ten points you cannot distinguish between the analytical and the numerical solutions. The analytical solution is scaled by the magnitude of Φ so you should explore the impact of how steep the curve for c is on the necessary number of collocation points. One can always select a large number of collocation points and simply be patient while the computer churns away; having a sense of the steepness of the curves being approximated helps in selecting a number of collocation points.

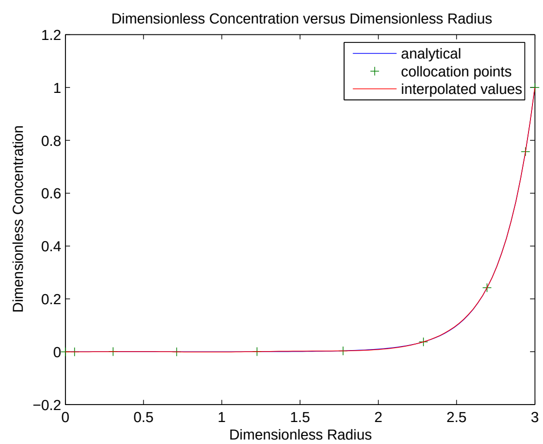

Figure 2: Numerical solution for ten collocation points and the analytical solution when $\Phi = 5$.