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ANALYTICAL SOLUTIONS FOR BOUNDARY VALUE PROBLEMS USING MAPLE

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INTRODUCTION

Using analytical solutions in chemical engineering education helps students who make quantitative predictions. One of the main reasons is that analytical solutions are exact solutions. This guarantees that the resulting quantitative predictions are accurate.

We present here an analytical solution method using Maple™ to solve systems of second-order linear ordinary differential equations in single and multiple domains. We start by reducing the order of the differential equations by assuming that the first-order derivative is an additional dependent variable.[1] This reduction yields a set of linear first-order differential equations that includes all the dependent variables (e.g., concentration), the first-order derivatives of the dependent variables (e.g., flux), and the parameters of the system. These equations can be solved by finding the matrix exponential [2] and symbolically integrating the resulting system of equations using Maple. Our method is similar to our previously presented analytical method for solving initial value problems (IVPs).[3] The method presented here is an extension to the previous method and is valid for various boundary conditions and constraints for boundary value problems (BVPs) in single and multiple domains.

First, the methodology is illustrated using a general second-order linear differential equation with generalized boundary conditions. Once the solution is obtained, we explain how this solution can be used to generate solutions for linear problems from chemical engineering.[4] Next, the methodology for solving boundary value problems with boundary conditions that require an additional constraint is illustrated by solving a boundary value problem with similar flux conditions at the boundaries in a lithium/polymer battery cell.[5] Finally, we demonstrate the methodology for a similar BVP with multiple domains that requires a multiple domain constraint equation by solving the coupled equations for the steady-state analysis of a lithium/polymer cell under uniform current distribution [6], and we used COMSOL to verify our solution. We present the model equations and their solutions in the body of our paper and the Maple solutions are available upon request from the authors.

ANALYTICAL METHOD FOR LINEAR ORDINARY DIFFERENTIAL EQUATIONS

First consider the second order linear ordinary differential equations (ODE) of the following form:

$$\frac{d^2\theta}{dx^2} + p\frac{d\theta}{dx} + q\theta = f(x) \qquad (1)$$

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where p and q are constants, with the following boundary conditions

$$k_1 \frac{d\theta}{dx} + h_1 \theta = c_1, \quad \text{at} \quad x = 0 \tag{2}$$

$$k_2 \frac{d\theta}{dx} + h_2 \theta = c_2, \quad \text{at} \quad x = 1 \tag{3}$$

Let $y_1 = \theta$ and $y_2 = \frac{d\theta}{dx}$, so that the governing equation can be transformed into the following system of equations:

$$\frac{dy_1}{dx} - y_2 = 0 \tag{4}$$

$$\frac{dy_2}{dx} + py_2 + qy_1 = f(x) \tag{5}$$

Equations 4 - 5 can be written in matrix form:

$$\frac{d\mathbf{y}}{dx} + \mathbf{A}\mathbf{y} = \mathbf{b}(x) \tag{6}$$

where $\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$ and $\mathbf{A} = \begin{bmatrix} 0 & -1 \\ q & p \end{bmatrix}$, $\mathbf{b}(x) = \begin{bmatrix} 0 \\ f(x) \end{bmatrix}$. Let $\mathbf{y}_0 = \mathbf{y}|_{x=0}$ and $\mathbf{y}_1 = \mathbf{y}|_{x=1}$ so that the boundary conditions can be written as

$$\mathbf{C}\mathbf{y}_0 + \mathbf{D}\mathbf{y}_1 = \mathbf{c} \tag{7}$$

where $\mathbf{C} = \begin{bmatrix} h_1 & k_1 \\ 0 & 0 \end{bmatrix}$, $\mathbf{D} = \begin{bmatrix} 0 & 0 \\ h_2 & k_2 \end{bmatrix}$, and $\mathbf{c} = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$. A useful solution of Equation 6 can be obtained by the integration factor method for multiple unknowns as given in Ref. [2].

$$\mathbf{y} = \exp(-\mathbf{A}x)\,\mathbf{y}_0 + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}(\lambda)\,d\lambda \tag{8}$$

where λ is a dummy variable in integration and $\exp(-\mathbf{A}x))$ is the matrix exponential. Recall that the matrix exponential of a square matrix (i.e., $\exp(\mathbf{A})$) can be expressed by a Taylor expression given by

$$\exp(\mathbf{A}) = \mathbf{I} + \frac{1}{1!}\mathbf{A} + \frac{1}{2!}\mathbf{A}^2 + \frac{1}{3!}\mathbf{A}^3 + ... \tag{9}$$

where I is the identity matrix with same dimensions as A. Equation 9 can be used to find the matrix exponential or a command in Maple can be used. Equation 8 yields at $x = 1$,

$$\mathbf{y}_1 = \exp(-\mathbf{A})\,\mathbf{y}_0 + \mathbf{f} \tag{10}$$

where $\mathbf{f} = \int_0^1 \exp[-\mathbf{A}(1-\lambda)]\,\mathbf{b}(\lambda)\,d\lambda$. Next, substitute Equation 10 into Equation 7 to obtain

$$\mathbf{C}\mathbf{y}_0 + \mathbf{D}[\exp(-\mathbf{A})\,\mathbf{y}_0 + \mathbf{f}] = \mathbf{c} \tag{11}$$

From Equation 11 we can obtain

$$\mathbf{y}_0 = [\mathbf{C} + \mathbf{D}\,\exp(-\mathbf{A})]^{-1}(\mathbf{c} - \mathbf{D}\,\mathbf{f}) \tag{12}$$

Now, substitute Equation 12 into Equation 8 to get the solution

$$\mathbf{y} = \exp(-\mathbf{A}x)\,[\mathbf{C} + \mathbf{D}\,\exp(-\mathbf{A})]^{-1}(\mathbf{c} - \mathbf{D}\,\mathbf{f}) + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}(\lambda)\,d\lambda \tag{13}$$

Thus, an analytical solution is obtained for the general linear second order differential equation and boundary conditions. Equations 1-13 can be modeled easily in Maple.

ILLUSTRATIVE EXAMPLES

Example 1: Irreversible Homogeneous Reaction in a Liquid

We demonstrate the method for linear problems by solving a general diffusion equation from chemical engineering. Consider the first order, irreversible conversion of species *A* to *B* in a stationary liquid film. The governing differential equation,[4] page 54 - 56, in dimensionless form is

$$\frac{d^2\theta}{d\eta^2} - Da\theta = 0 \tag{14}$$

subject to the following boundary conditions,

$$\frac{d\theta}{d\eta}(0) = 0 \tag{15}$$

$$\theta(1) = 1 \tag{16}$$

where θ is the dimensionless concentration, η is the dimensionless distance, $Da = \frac{k_V L^2}{D_A}$ is the Damköhler number for reaction relative to diffusion, D_A is the diffusion coefficient of species *A*, k_V is the rate constant, and *L* is the charateristic length. The stationary liquid film is chosen because it is linear and has an analytical solution.

$$\theta(\eta) = \frac{\cosh\left(\sqrt{Da}\eta\right)}{\cosh\left(\sqrt{Da}\right)} \tag{17}$$

Equation 14 can be written in the form of a vector differential Equation 6, where

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \theta \\ \frac{d\theta}{dx} \end{bmatrix} \tag{18}$$

$$\mathbf{A} = \begin{bmatrix} 0 & -1 \\ -Da & 0 \end{bmatrix} \tag{19}$$

$$\mathbf{C} = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \quad \mathbf{D} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix} \quad \text{and} \quad \mathbf{c} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{20}$$

The general solution presented in Equation 13 is valid for the BVP. For this example, the forcing function $\mathbf{b}(\lambda)$ is zero; as a result, $\mathbf{f}$ is also zero. Substituting the $\mathbf{b}(\lambda)$, $\mathbf{f}$ in Equation 13 simplifies to the following equation

$$\mathbf{y} = \exp(-\mathbf{A}x)\left[\mathbf{C} + \mathbf{D}\exp(-\mathbf{A})\right]^{-1}(\mathbf{c}) \tag{21}$$

Hence, by substituting Equation 19 - 20 into Equation 21 we get,

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} \theta \\ \frac{d\theta}{dx} \end{bmatrix} = \begin{bmatrix} \frac{\exp\left(\sqrt{Da}\eta\right)+\exp\left(-\sqrt{Da}\eta\right)}{\exp\left(\sqrt{Da}\right)+\exp\left(-\sqrt{Da}\right)} \\ \frac{\sqrt{Da}\exp\left(\sqrt{Da}\eta\right)+\sqrt{Da}\exp\left(-\sqrt{Da}\eta\right)}{\exp\left(\sqrt{Da}\right)+\exp\left(-\sqrt{Da}\right)} \end{bmatrix} \tag{22}$$

From the first row of the matrix, θ is obtained as

$$\theta = \frac{\exp\left(\sqrt{Da}\eta\right) + \exp\left(-\sqrt{Da}\eta\right)}{\exp\left(\sqrt{Da}\right) + \exp\left(-\sqrt{Da}\right)} = \frac{\cosh\left(\sqrt{Da}\eta\right)}{\cosh\left(\sqrt{Da}\right)} \tag{23}$$

which is the same as Equation 17.

Example 2: Reversible Homogeneous Reaction in a Liquid

Consider the reversible conversion of species *A* to *B* in a stationary liquid film. The governing differential equations,[4] pages 57 - 59, are

$$D_A \frac{d^2 C_A}{dy^2} + k_{-1} C_B - k_1 C_A = 0, \quad D_B \frac{d^2 C_B}{dy^2} - k_{-1} C_B + k_1 C_A = 0 \tag{24}$$

subject to the following boundary conditions

$$C_A(0) = C_{A0}, \quad C_B(0) = C_{B0} \tag{25}$$

$$\frac{dC_A}{dy}(L) = 0, \quad \frac{dC_B}{dy}(L) = 0 \tag{26}$$

Using the dimensionless variables

$$\eta = \frac{y}{L}, \quad \theta_A = \frac{C_A}{C_{A0}}, \quad \theta_B = \frac{KC_B}{C_{A0}}, \quad K = \frac{k_{-1}}{k_1} \tag{27}$$

Equation 24 coverts to

$$\frac{d^2 C_A}{d\eta^2} + \frac{L^2}{D_A}(k_{-1} C_B - k_1 C_A) = 0, \quad \frac{d^2 C_B}{d\eta^2} - \frac{L^2}{D_B}(k_{-1} C_B - k_1 C_A) = 0 \tag{28}$$

or

$$\frac{1}{C_{A0}} \frac{d^2 C_A}{d\eta^2} + \frac{k_1 L^2}{D_A}\left(\frac{k_{-1} C_B}{k_1 C_{A0}} - \frac{C_A}{C_{A0}}\right) = 0, \quad \frac{1}{C_{A0}} \frac{d^2 C_B}{d\eta^2} - \frac{k_{-1} L^2}{D_B}\left(\frac{C_B}{C_{A0}} - \frac{k_1 C_A}{k_{-1} C_{A0}}\right) = 0 \tag{29}$$

Let the dimensionless parameters be

$$\alpha = \frac{k_1 L^2}{D_A}, \quad \beta = \frac{k_{-1} L^2}{D_B}, \quad \gamma = \frac{KC_{B0}}{C_{A0}} \tag{30}$$

Equation 29 then converts to

$$\frac{d^2 \theta_A}{d\eta^2} + \alpha(\theta_B - \theta_A) = 0, \quad \frac{d^2 \theta_B}{d\eta^2} - \beta(\theta_B - \theta_A) = 0 \tag{31}$$

Boundary conditions from Equations 25 and 26 then convert to

$$\theta_A(0) = 1, \quad \theta_B(0) = \gamma \tag{32}$$

$$\frac{d\theta_A}{d\eta}(1) = 0, \quad \frac{d\theta_B}{d\eta}(1) = 0 \tag{33}$$

The final solution for this case can be obtained by substituting $\mathbf{A} = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -\alpha & \alpha & 0 & 0 \\ \beta & \beta & 0 & 0 \end{bmatrix}$, $\mathbf{C} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$, $\mathbf{D} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$, $\mathbf{b} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$ and $\mathbf{c} = \begin{bmatrix} 1 \\ \gamma \\ 0 \\ 0 \end{bmatrix}$ into Equation 13. For brevity, the final solution is not given here and is the same as Equations 3.2-24 - 3.2-25 in Ref. [4].

Example 3: Jump Condition for Dopant Concentration C at a Melt/Crystal Interface

Consider a continuous solidification process. The governing differential equation [4], page 64 - 66, is,

$$D\frac{d^2C}{dx^2} - U\frac{dC}{dx} = 0 \tag{34}$$

$$C_s = KC(\delta) \tag{35}$$

with the boundary conditions

$$C(0) = C_\infty \tag{36}$$

$$UC(\delta) - D\frac{dC}{dx}(\delta) = UC_s \tag{37}$$

where D is the diffusion coefficient, U is the velocity of the melt/solid, K is the solid/melt equilibrium partition coefficient for the dopant, and δ is the stationary melt/solid interface. Using Equation 35 to eliminate C_s from Equation 37, the interfacial balance becomes

$$U(1-K)C(\delta) - D\frac{dC}{dx}(\delta) = 0 \tag{38}$$

The final solution for this case can be obtained by substituting $\mathbf{A} = \begin{bmatrix} 0 & -1 \\ 0 & -\frac{U}{D} \end{bmatrix}$, $\mathbf{C} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$, $\mathbf{D} = \begin{bmatrix} 0 & 0 \\ U(1-K) & -D \end{bmatrix}$ $\mathbf{b} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$, and $\mathbf{c} = \begin{bmatrix} C_\infty \\ 0 \end{bmatrix}$ into Equation 13. Hence the analytical solution of Equation 34 that satisfies boundary conditions 36 and 38 is

$$C(y) = C_\infty \frac{K + (1-K)e^{\frac{(x-\delta)U}{D}}}{K + (1-K)e^{\frac{-U\delta}{D}}} \tag{39}$$

Equation 39 can be rewritten using dimensionless parameters $\theta = \frac{C}{C_\infty}$, $\eta = \frac{y}{\delta}$ and $Pe = \frac{U\delta}{D}$ as

$$\theta(\eta) = \frac{K + (1-K)e^{Pe(\eta-1)}}{K + (1-K)e^{-Pe}} \tag{40}$$

where *Pe* is the Peclet number for the dopant.

Example 4: Monroe and Newman Dendrite Growth Model: Steady State Solution

Monroe and Newman [5] presented a dendrite growth model in a parallel elctrode lithium/polymer cell during galvanostatic charging. The steady state concentration profiles in their cell is given by

$$D\frac{d^2c}{dx^2} = 0 \tag{41}$$

with the boundary condition

$$\frac{dc}{dx} = \frac{-i\left(1-t_+^0\right)}{DF}, \quad @ \quad x = 0 \tag{42}$$

and the contraint equation

$$\int_0^L c(x)\,dx = c_b L \tag{43}$$

where t_+^0 is the transference number, F is Faraday's constant, c_b is the bulk concentration, and L is the length of the cell. See Ref. [5]. Note that the boundary condition at $x = L$ would be the same as Equation 42 with a positive sign and would consequently not provide sufficient information to obtain a solution. Instead, we must invoke conservation of mass or moles in this case since there is no homogeneous reaction. The constraint equation for this model, Equation 43, expresses conservation of mass or moles in this case. Now, let $y_1 = c$ and $y_2 = \frac{dc}{dx}$, and the governing equation becomes the following equation system

$$\frac{dy_1}{dx} = y_2 \tag{44}$$

$$\frac{dy_2}{dx} = 0 \tag{45}$$

Rewrite Equation 44 and Equation 45

$$\frac{d}{dx}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} + \begin{bmatrix} 0 & -1 \\ 0 & 0 \end{bmatrix}\begin{bmatrix} y_1 \\ y_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{46}$$

Let $\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix}$, $\mathbf{A} = \begin{bmatrix} 0 & -1 \\ 0 & 0 \end{bmatrix}$, and $\mathbf{b} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$, the equation system can be expressed with the matrix

$$\frac{d\mathbf{y}}{dx} + \mathbf{A}\mathbf{y} = \mathbf{b} \tag{47}$$

The general form of the solution is obtained from Equation 47 is

$$\mathbf{y} = \exp(-\mathbf{A}x)\,\mathbf{y}_0 + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda \tag{48}$$

Let $\mathbf{y}_0 = \mathbf{y}|_{x=0}$ and $\mathbf{y}_c = \int_0^L \mathbf{y}dx$ and obtain

$$\mathbf{y}_c = \int_0^L \mathbf{y}dx = \int_0^L \exp(-\mathbf{A}x)\,\mathbf{y}_0 dx + \int_0^L \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda dx \tag{49}$$

Equation 49 can be rewritten as

$$\begin{bmatrix} \int_0^L \exp(-\mathbf{A}x)\,dx & -\mathbf{I} \end{bmatrix}\begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_c \end{bmatrix} = -\int_0^L \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda dx \tag{50}$$

Equation 42 becomes:

$$\begin{bmatrix} 0 & 1 \end{bmatrix}\mathbf{y}_0 = -\frac{i\left(1-t_+^0\right)}{DF} \tag{51}$$

Equations 43 becomes:

$$\begin{bmatrix} 1 & 0 \end{bmatrix}\mathbf{y}_c = c_b L \tag{52}$$

In this case $\mathbf{C} = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$, $\mathbf{D} = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$, and $\mathbf{c} = \begin{bmatrix} -\frac{i\left(1-t_+^0\right)}{DF} \\ c_b L \end{bmatrix}$

Equations 51 and Equation 52 put together become

$$\begin{bmatrix} \mathbf{C} & \mathbf{D} \end{bmatrix}\begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_c \end{bmatrix} = \mathbf{c} \tag{53}$$

From Equation 50 and Equation 53, the entire equation system can be expressed as:

$$\begin{bmatrix} \int_0^L \exp(-\mathbf{A}x)\,dx & -\mathbf{I} \\ \mathbf{C} & \mathbf{D} \end{bmatrix}\begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_c \end{bmatrix} = \begin{bmatrix} -\int_0^L \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda dx \\ \mathbf{c} \end{bmatrix} \tag{54}$$

Let $\mathbf{M} = \begin{bmatrix} \int_0^L \exp(-\mathbf{A}x)\,dx & -\mathbf{I} \\ \mathbf{C} & \mathbf{D} \end{bmatrix}$, and $\mathbf{n} = \begin{bmatrix} -\int_0^L \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda dx \\ \mathbf{c} \end{bmatrix}$

Equation 54 can be simplified to

$$\mathbf{M}\begin{bmatrix}\mathbf{y}_0\\ \mathbf{y}_c\end{bmatrix} = \mathbf{n} \tag{55}$$

From Equation 55

$$\begin{bmatrix}\mathbf{y}_0\\ \mathbf{y}_c\end{bmatrix} = \mathbf{M}^{-1}\mathbf{n} \tag{56}$$

$$\mathbf{y}_0 = \begin{bmatrix}\mathbf{I} & \mathbf{0}\end{bmatrix}\mathbf{M}^{-1}\mathbf{n} \tag{57}$$

Substituting $\mathbf{y}_0$ from Equation 57 into Equation 48 gives

$$\mathbf{y} = \exp(-\mathbf{A}x)\begin{bmatrix}\mathbf{I} & \mathbf{0}\end{bmatrix}\mathbf{M}^{-1}\mathbf{n} + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda \tag{58}$$

$$c = y_1 = \begin{bmatrix}1 & 0\end{bmatrix}\mathbf{y} = \begin{bmatrix}1 & 0\end{bmatrix}\left[\exp(-\mathbf{A}x)\begin{bmatrix}\mathbf{I} & \mathbf{0}\end{bmatrix}\mathbf{M}^{-1}\mathbf{n} + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda\right] \tag{59}$$

The analytical solution obtained after using the matrix exponential method is

$$c(x) = c_b + \frac{i(L-2x)\left(1-t_+^0\right)}{2DF} \tag{60}$$

Example 5: Doyle and Newman Simplified Model: Steady State Solutions

Doyle and Newman[6] presented a simplified model in a Lithium/polymer cell sandwich consisting of a separator and a porous cathode electrode during galvanostatic discharging (Figure 1).

The extra constraint for this model is the overall mass or mole balance (since no chemical reactions are occurring). This constraint can be derived based on the cross-sectional area, A (i.e., the projected area of the separator and electrode) of the cell, the thickness of the separator, L_s, the thickness of the positive electrode, L_+, the porosities of the porous electrode ϵ, and the initial concentration, c_0 (moles per volume of pores filled with electrolyte in the separator and the porous electrode). Once a current is impressed on the lithium metal anode and the lithium ion consumption reaction occurs within the porous cathode, the following mole balance must apply:

$$A\int_0^{L_s} c_1(x)\,dx + A\int_{L_s}^{L_s+L_+} \epsilon c_2(x)\,dx = Ac_0L_s\left(1.0 + \epsilon\frac{L_+}{L_s}\right) \tag{61}$$

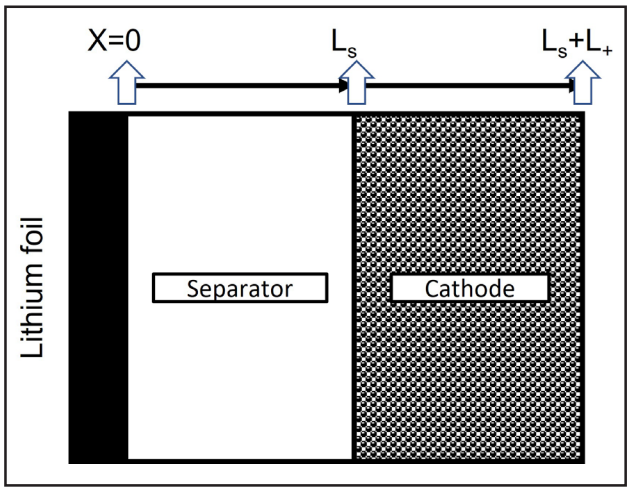

Figure 1. *Schematic diagram of the Lithium/polymer cell.*

where the subscripts 1 and 2 refer to the separator and the cathode, respectively. The steady state concentration profiles in the separator is given by

$$D\frac{\partial^2 c_1}{\partial x^2} = 0 \tag{62}$$

The material balance for the porous electrode is an equation based concentrated solution theory and porous electrode theory.[7] The steady-state equation for the *x* direction only is

$$\epsilon^{3/2}D\frac{\partial^2 c_2}{\partial x^2} + aj_n\left(1-t_+^0\right) = 0 \tag{63}$$

where the pore wall flux, j_n, is assumed to be a constant. The boundary condition a *x* = 0 can be written for our binary electrolyte as (see Ref.[7])

$$\frac{AD}{\left(1-t_+^0\right)}\frac{\partial c_1}{\partial x}\bigg|_{x=0} = -A\frac{I}{F} \tag{64}$$

where I is the current density based on the projected area of the electrode, A. Also, D is the binary electrolyte diffusion coefficient, and t_+^0 is the cation transference number with respect to the solvent velocity. The boundary condition at $x = L_s + L_+$ is as follows:

$$\left.\frac{\partial c_2}{\partial x}\right|_{x=L_s+L_+} = 0 \tag{65}$$

Finally, continuity of flux and concentration of the binary electrolyte from the separator to the porous electrode at $x = L_s$ lead to

$$-\left.\frac{D}{\left(1-t_+^0\right)}\frac{\partial c_1}{\partial x}\right|_{x=L_s} = -\left.\frac{D\epsilon^{3/2}}{\left(1-t_+^0\right)}\frac{\partial c_2}{\partial x}\right|_{x=L_s} \tag{66}$$

$$c_1 = c_2 \quad \text{at} \quad x = L_s \tag{67}$$

Equation 61 can be written in dimensionless form using the dimensionless variables:

$$\int_0^1 L_s\Theta_1\left(X_1\right)dX_1 + \int_0^1 \epsilon L_+\Theta_2\left(X_2\right)dX_2 = L_s\left(1+\epsilon\frac{L_+}{L_s}\right) \tag{68}$$

where

$$\Theta_1\left(X_1\right) = \frac{c_1}{c_0}, \Theta_2\left(X_2\right) = \frac{c_2}{c_0}, \quad X_1 = \frac{x}{L_s}, X_2 = \frac{x-L_s}{L_+}, \quad \tau_1 = \frac{Dt}{L_s^2}, \tau_2 = \frac{Dt}{L_+^2}, J = \frac{a\left(1-t_+^0\right)L_+^2 j_n}{\epsilon D c_0} \tag{69}$$

Also note that once we start passing current from the lithium metal electrode into the separator, the dimensionless concentration will be greater than 1 in the separator, and the dimensionless concentration in the porous electrode will be less than ϵr. The reason this extra constraint is needed can be seen by solving the steady-state model equations using the classical method. Substitution of the variables in Equation 69 into Equation 62 yields the dimensionless governing equation in the separator:

$$\frac{\partial^2\Theta_1}{\partial X_1^2} = 0 \tag{70}$$

Substitution of the variables in Equation 69 into Equation 63 yields the dimensionless governing equation in the porous electrodes:

$$\epsilon^{1/2}\frac{\partial^2\Theta_2}{\partial X_2^2} + J = 0 \tag{71}$$

The boundary condition at $x = 0$ given by Equation 64 becomes:

$$\left.\frac{\partial\Theta_1}{\partial X_1}\right|_{X_1=0} = -\gamma \quad \text{where} \quad \gamma = \frac{I\left(1-t_+^0\right)L_s}{FDc_0} \tag{72}$$

Equation 65, in terms of dimensionless variables, becomes

$$\left.\frac{\partial\Theta_2}{\partial X_2}\right|_{X_2=1} = 0 \tag{73}$$

The continuity of flux from the separator to the porous electrode given in Equation 66 becomes in dimensionless form

$$\left.\frac{1}{L_s}\frac{\partial\Theta_1}{\partial X_1}\right|_{X_1=1} = \left.\frac{\epsilon^{3/2}}{L_+}\frac{\partial\Theta_2}{\partial X_2}\right|_{X_2=0} \tag{74}$$

X_1 and X_2 are independent variables that can be replaced by a single dummy variable x. Also note that according to Equation 69, we have continuity of the dependent variable at the interface between the separator and the porous electrode, which becomes in dimensionless form

$$\Theta_1\left(1\right) = \Theta_2\left(0\right) \tag{75}$$

Let $y_1 = \Theta_1$, $y_2 = \Theta_2$, $y_3 = \frac{d\Theta_1}{dx}$, and $y_4 = \frac{d\Theta_2}{dx}$ and the steady-state governing Equations 62 and 63 become the following system of equations

$$\frac{dy_1}{dx} = y_3 \tag{76}$$

$$\frac{dy_2}{dx} = y_4 \tag{77}$$

$$\frac{dy_3}{dx} = 0 \tag{78}$$

$$\frac{dy_4}{dx} = -\frac{J}{\epsilon^{1/2}} \tag{79}$$

Rewrite Equations 76 - 79 as

$$\frac{d}{dx}\begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix} + \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -\frac{J}{\epsilon^{1/2}} \end{bmatrix} \tag{80}$$

Let $\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix}$, $\mathbf{A} = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$, and $\mathbf{b} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ -\frac{J}{\epsilon^{1/2}} \end{bmatrix}$, the equation system can be expressed with the matrix format

$$\frac{d\mathbf{y}}{dx} + \mathbf{A}\mathbf{y} = \mathbf{b} \tag{81}$$

The general form of the solution is obtained from Equation 81

$$\mathbf{y} = \exp(-\mathbf{A}x)\,\mathbf{y}_0 + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}(\lambda)\,d\lambda \tag{82}$$

Let $\mathbf{y}_0 = \mathbf{y}|_{x=0}$, $\mathbf{y}_1 = \mathbf{y}|_{x=1}$ and $\mathbf{y}_c = \int_0^1 \mathbf{y}dx$ and obtain

$$\mathbf{y}_1 = \exp(-\mathbf{A}x)\,\mathbf{y}_0 + \int_0^1 \exp[-\mathbf{A}(1-t)]\,\mathbf{b}(\lambda)\,d\lambda \tag{83}$$

$$\mathbf{y}_c = \int_0^1 \mathbf{y}dx = \int_0^1 \exp(-\mathbf{A}x)\,\mathbf{y}_0 dx + \int_0^1\int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}(\lambda)\,d\lambda dx \tag{84}$$

Equation 83 and Equation 84 are rewritten as

$$\begin{bmatrix} \exp(-\mathbf{A}) & -\mathbf{I} & \mathbf{0} \\ \int_0^1 \exp(-\mathbf{A}x)\,dx & \mathbf{0} & -\mathbf{I} \end{bmatrix} \begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_1 \\ \mathbf{y}_c \end{bmatrix} = \begin{bmatrix} -\int_0^1 \exp[-\mathbf{A}(1-\lambda)]\,\mathbf{b}d\lambda \\ -\int_0^1\int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda dx \end{bmatrix} \tag{85}$$

Equations 72 and Equation 73 are expressed as

$$\begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \mathbf{y}_0 = \begin{bmatrix} -\gamma \\ 0 \end{bmatrix} \tag{86}$$

Equations 72 and Equation 73 are expressed as

$$\begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \mathbf{y}_1 = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{87}$$

Equation 85 is expressed as

$$\begin{bmatrix} L_s & \epsilon L_+ & 0 & 0 \end{bmatrix} \mathbf{y}_c = L_s \left(1 + \epsilon \frac{L_+}{L_s}\right) \tag{88}$$

Let $\mathbf{C} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$, $\mathbf{D} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \end{bmatrix}$, $\mathbf{E} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ L_s & \epsilon L_+ & 0 & 0 \end{bmatrix}$, and $\mathbf{c} = \begin{bmatrix} -\gamma \\ 0 \\ 0 \\ L_s \left(1 + \epsilon \frac{L_+}{L_s}\right) \end{bmatrix}$

Equations 86 - 88 can be put together

$$\begin{bmatrix} \mathbf{C} & \mathbf{D} & \mathbf{E} \end{bmatrix} \begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_1 \\ \mathbf{y}_c \end{bmatrix} = \mathbf{c} \tag{89}$$

From Equation 85 and Equation 89, the entire system is expressed as:

$$\begin{bmatrix} \exp(-\mathbf{A}) & -\mathbf{I} & \mathbf{0} \\ \int_0^1 \exp(-\mathbf{A}x)\, dx & \mathbf{0} & -\mathbf{I} \\ \mathbf{C} & \mathbf{D} & \mathbf{E} \end{bmatrix} \begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_1 \\ \mathbf{y}_c \end{bmatrix} = \begin{bmatrix} -\int_0^1 \exp[-\mathbf{A}(1-\lambda)]\, \mathbf{b}(\lambda)\, d\lambda \\ -\int_0^1 \int_0^x \exp[-\mathbf{A}(x-\lambda)]\, \mathbf{b}(\lambda)\, d\lambda dx \\ \mathbf{c} \end{bmatrix} \tag{90}$$

Let M = $\begin{bmatrix} \exp(-\mathbf{A}) & -\mathbf{I} & \mathbf{0} \\ \int_0^1 \exp(-\mathbf{A}x)\, dx & \mathbf{0} & -\mathbf{I} \\ \mathbf{C} & \mathbf{D} & \mathbf{E} \end{bmatrix}$, and $\mathbf{n} = \begin{bmatrix} -\int_0^1 \exp[-\mathbf{A}(1-\lambda)]\, \mathbf{b}(\lambda)\, d\lambda \\ -\int_0^1 \int_0^x \exp[-\mathbf{A}(x-\lambda)]\, \mathbf{b}(\lambda)\, d\lambda dx \\ \mathbf{c} \end{bmatrix}$,

Equation 90 is simplified as

$$\mathbf{M} \begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_1 \\ \mathbf{y}_c \end{bmatrix} = \mathbf{b} \tag{91}$$

From Equation 91

$$\begin{bmatrix} \mathbf{y}_0 \\ \mathbf{y}_1 \\ \mathbf{y}_c \end{bmatrix} = \mathbf{M}^{-1}\mathbf{n} \tag{92}$$

$$\mathbf{y}_0 = \begin{bmatrix} \mathbf{I} & \mathbf{0} & \mathbf{0} \end{bmatrix} \mathbf{M}^{-1}\mathbf{n} \tag{93}$$

Substituting $\mathbf{y}_0$ from Equation 93 in Equation 82 gives

$$\mathbf{y} = \exp(-\mathbf{A}x) \begin{bmatrix} \mathbf{I} & \mathbf{0} & \mathbf{0} \end{bmatrix} \mathbf{M}^{-1}\mathbf{n} + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\, \mathbf{b} d\lambda \tag{94}$$

$$\Theta_1 = \begin{bmatrix} 1 & 0 & 0 & 0 \end{bmatrix} \mathbf{y} = \begin{bmatrix} 1 & 0 & 0 & 0 \end{bmatrix} \left[\exp(-\mathbf{A}x) \begin{bmatrix} \mathbf{I} & \mathbf{0} & \mathbf{0} \end{bmatrix} \mathbf{M}^{-1}\mathbf{n} + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda \right] \quad (95)$$

$$\Theta_2 = \begin{bmatrix} 0 & 1 & 0 & 0 \end{bmatrix} \mathbf{y} = \begin{bmatrix} 0 & 1 & 0 & 0 \end{bmatrix} \left[\exp(-\mathbf{A}x) \begin{bmatrix} \mathbf{I} & \mathbf{0} & \mathbf{0} \end{bmatrix} \mathbf{M}^{-1}\mathbf{n} + \int_0^x \exp[-\mathbf{A}(x-\lambda)]\,\mathbf{b}d\lambda \right] \quad (96)$$

Thus, dimensionless concentration profiles obtained using Maple are

$$\Theta_1 = -\frac{JL_+\sqrt{\epsilon}}{3(\epsilon L_+ + L_s)} + \frac{(2\epsilon L_+ + L_s)\gamma}{2(\epsilon L_+ + L_s)} + \frac{L_s\left(1+\epsilon\frac{L_+}{L_s}\right)}{\epsilon L_+ + L_s} - x\gamma \quad (97)$$

$$\Theta_2 = -\frac{JL_+\sqrt{\epsilon}}{3(\epsilon L_+ + L_s)} - \frac{L_s\gamma}{2(\epsilon L_+ + L_s)} + \frac{L_s\left(1+\epsilon\frac{L_+}{L_s}\right)}{\epsilon L_+ + L_s} + \frac{(x-1)J}{\sqrt{\epsilon}r} - \frac{(x-1)^2 J}{2\sqrt{\epsilon}r^2} \quad (98)$$

These equations are the same as Equations 17 and 18 of Doyle and Newman [6] with the following sign changes to fix a typo in the original paper; the second minus sign in their Equation 19 needs to be changed to a plus sign, and the first minus sign in their Equation 20 needs to be changed to a plus sign.

Steady-state concentration profiles at various current densities for the model system described above are solved by using the method of exponential matrix are given in Figure 2. Note that the concentration at the end of the porous electrode is not driven to zero at the steady-state because of the usage of the extra constraint 61.

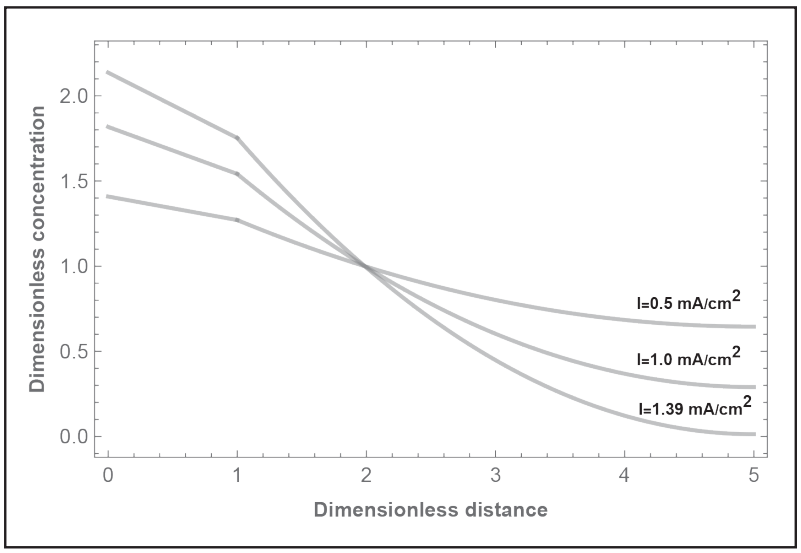

Figure 2. *Steady-state concentration profiles across the full cell for galvanostatic discharges at various current densities by using method of exponential matrix.*

CONCLUSIONS

An analytic solution method has been presented for solving single or multiple dependent variable second-order linear BVPs in single and multiple domains. The presented method is straightforward and provides a general solution, valid for different boundary conditions and constraints. Furthermore, the method can solve nonlinear and time-dependent problems using the semi-analytic technique.[8,9] Maple worksheets used for obtaining the results in this paper are available upon request from the authors at white@cec.sc.edu.

REFERENCES

1. Rice RG and Do DD (2012) Applied Mathematics and Modeling for Chemical Engineers. John Wiley & Sons, New York, NY.
2. Varma A and Morbidelli M (1997) Mathematical Methods in Chemical Engineering. Oxford University Press. New York.
3. Subramanian VR and White RE (2000) Solving differential equations with maple. *Chemical Engineering Education*. 34(4): 328–336. https://journals.flvc.org/cee/article/view/123036. Accessed Nov 21, 2023.
4. Deen WM (2012) Analysis of Transport Phenomena, 2nd ed. Oxford University Press, New York, NY.
5. Monroe C and Newman J (2003) Dendrite growth in lithium/polymer systems: A propagation model for liquid electrolytes under galvanostatic conditions. *Journal of The Electrochemical Society*. 150(10): A1377. DOI: 10.1149/1.1606686
6. Doyle M and Newman J (1997) Analysis of capacity–rate data for lithium batteries using simplified models of the discharge process. *Journal of Applied Electrochemistry*. 27: 846–856. DOI: 10.1023/A:1018481030499.
7. Newman J and Thomas-Alyea KE (2012) Electrochemical systems. John Wiley & Sons, New York, NY.
8. De Vidts P and White RE (1992) A semi-analytical solution method for linear partial differential equations. *Computers & Chemical Engineering*. 16(10-11): 1007–1009 DOI: 10.1016/0098-1354(92)80032-5.
9. Subramanian VR and White RE (2000) A semianalytical method for predicting primary and secondary current density distributions: Linear and nonlinear boundary conditions. *Journal of the Electrochemical Society*. 147(5): 1636. DOI: 10.1149/1.1393410 .❑