

# Diffusion and heat transfer\*

James B. Rawlings<sup>†</sup>  
Department of Chemical and Biological Engineering  
University of Wisconsin-Madison  
Madison, WI 53706

September 1, 2014  
Copyright © 2014 by James B. Rawlings

## 1 Heat Conduction

**Temperature gradient and heat flux.** A temperature gradient produces a flux of heat as the heat flows from hot to cold. The rate at which this flow occurs is determined by the material property called the thermal conductivity,  $k$ . The empirical observation that the flux is linear in the gradient is known as Fourier's law of heat conduction

$$q = -k \frac{dT}{dx} \quad \text{Fourier's law of heat conduction} \quad (1)$$

in which  $q$  is the heat flux, energy per area per time,  $x$  is spatial position, and  $T$  is temperature. Notice the negative sign is required so that the heat flows from hot to cold.

**Energy and Energy balance.** Ignoring the kinetic and potential energies of the system, we consider the system total energy to be only the internal energy, denoted by  $U$ , which is the internal energy per volume. Consider the slab geometry depicted in Figure 1. If we take a small volume element of constant cross-sectional area  $A$  and width  $\Delta x$ , we can write a balance on the energy contained in this volume element. The energy changes due to heat conducted into the element through the face at location  $x$  and the heat conducted out of the element through the face at location  $x + \Delta x$

$$\frac{\partial (UA\Delta x)}{\partial t} = qA|_x - qA|_{x+\Delta x}$$

---

\*See Bird, Stewart, and Lightfoot (2002, Ch. 12, 19)

<sup>†</sup>rawlings@engr.wisc.edu

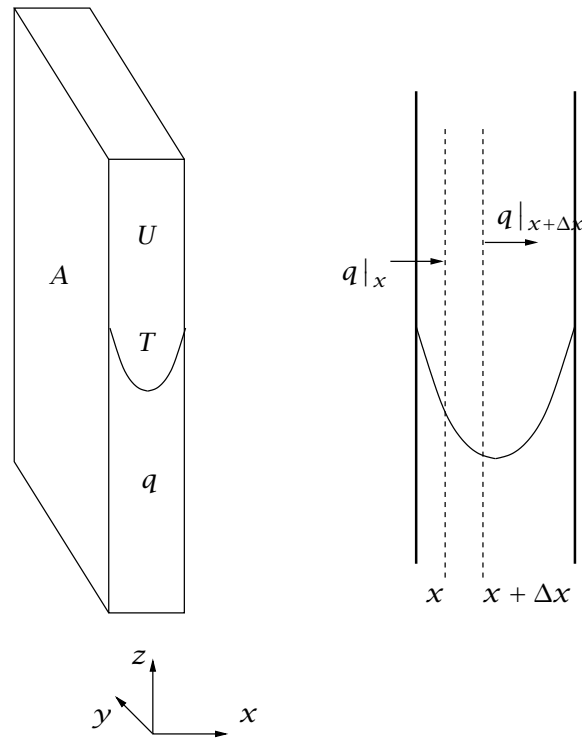


Figure 1: One-dimensional heat conduction in the slab geometry. The right-hand side shows a volume element considered in the energy balance.

Dividing both sides by  $A\Delta x$  and rearranging gives

$$\frac{\partial U}{\partial t} = -\frac{q|_{x+\Delta x} - q|_x}{\Delta x}$$

and taking the limit as  $\Delta x \rightarrow 0$  gives

$$\frac{\partial U}{\partial t} = -\frac{\partial}{\partial x} q \quad (2)$$

For a single-phase system, the temperature, pressure, and chemical composition determine all intensive properties of the system, including the internal energy

$$U = U(T, P, c_j) \quad (3)$$

Changes in internal energy can be computed from changes in the temperature, pressure and chemical composition by

$$dU = \left(\frac{\partial U}{\partial T}\right)_{P,c_j} dT + \left(\frac{\partial U}{\partial P}\right)_{T,c_j} dP + \sum_j \left(\frac{\partial U}{\partial c_j}\right)_{T,P,c_k} dc_j$$

For the heat conduction process, we assume the pressure and chemical composition do not vary, so  $dT$  and  $dc_j$  are zero. The change in internal energy with temperature at constant pressure and composition is the definition of the (constant pressure) heat capacity,  $\hat{C}_P$

$$\hat{C}_P = \left(\frac{\partial U}{\partial T}\right)_{P,c_j}$$

The change in internal energy is therefore given by the simple expression

$$dU = \rho \hat{C}_P dT$$

So we have for the time derivative

$$\frac{\partial U}{\partial t} = \rho \hat{C}_P \frac{\partial T}{\partial t}$$

Substituting this relation for the internal energy and Fourier's law of heat conduction, Equation 1, for the flux into the energy balance, Equation 2, gives the heat conduction equation

$$\rho \hat{C}_P \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right)$$

If we next assume constant thermal properties we can take  $k$  outside the derivatives and we obtain

$$\boxed{\rho \hat{C}_P \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \quad \text{heat equation}} \quad (4)$$

Equation 4 is known as the heat equation. We next consider dimensionless variables and derive a dimensionless version of the heat equation.

### Example 1: Dimensionless variables

A solid slab of width  $2b$  is initially at temperature  $T_0$ . At time  $t = 0$ , the surfaces at  $x = \pm b$  are suddenly raised to temperature  $T_1$  and maintained at that temperature.

It is often convenient to create dimensionless variables before solving a problem. The benefit is often that many of the physical parameters can be combined into a smaller number of dimensionless parameters that describe the phenomenon of interest.

Choose dimensionless temperature, time, and position variables and rewrite the heat equation in the dimensionless variables.

**Solution**

The physical parameters appearing in the heat equation with the given boundary conditions are

Parameter	Units
$T_0, T_1$	K
$b$	l
$k$	energy/(t l K)
$\rho$	m/l <sup>3</sup>
$\hat{C}_p$	energy/(m K)

We have three variables in the problem, the dependent variable  $T$  and the two independent variables,  $x$  and  $t$ .

**Choosing dimensionless variables.** We nondimensionalize each of these variables in turn. First consider  $T$ . Denote dimensionless temperature by  $\Theta$ , and define it as follows

$$\Theta = \frac{T - T_0}{T_1 - T_0}$$

The slab initial condition,  $T = T_0$  translates to the dimensionless equation  $\Theta = 0$ . If the temperature reaches  $T = T_1$ , the corresponding dimensionless temperature is  $\Theta = 1$ .

Next consider the spatial position  $x$ . Denote dimensionless position as  $\xi$ , and define it as follows

$$\xi = \frac{x}{b}$$

The two boundaries of the slab are at  $x = \pm b$ , which corresponds to  $\xi = \pm 1$ .

Finally consider the time  $t$ . Let  $\tau$  denote a dimensionless time. Time is perhaps the least obvious variable to make dimensionless. But we see that since time appears explicitly in the thermal conductivity parameter  $k$ , we can use the other parameters to cancel out the other units. By inspection we see that the grouping  $k/(\rho\hat{C}_pb^2)$  has units of  $1/t$ . So we can define dimensionless time by

$$\tau = \frac{k}{\rho\hat{C}_pb^2}t$$

**Transforming the differential equation and boundary conditions.** Given the dimensionless variables, we now wish to transform the heat equation into a dimensionless heat equation for  $\Theta(\xi, \tau)$ . First substitute the dimensionless variables into the heat equation to obtain

$$\rho\hat{C}_p \frac{\partial ((T_1 - T_0)\Theta + T_0)}{\partial \left( \frac{\rho\hat{C}_pb^2}{k} \tau \right)} = k \frac{\partial^2 ((T_1 - T_0)\Theta + T_0)}{\partial (b\xi)^2}$$

We next note that we can pass the constant parameters outside the derivative and that the derivative of a constant parameter is zero, or,

$$\partial(c_1x + c_2) = c_1\partial x \quad \partial^2(c_1x + c_2) = c_1\partial^2x$$

Using this fact to simplify the previous equation gives

$$\frac{k}{b^2}(T_1 - T_0) \frac{\partial \Theta}{\partial \tau} = \frac{k}{b^2}(T_1 - T_0) \frac{\partial^2 \Theta}{\partial \xi^2}$$

Simplifying this result gives the dimensionless heat equation

$\frac{\partial \Theta}{\partial \tau} = \frac{\partial^2 \Theta}{\partial \xi^2} \quad \text{dimensionless heat equation}$
---

Notice that no parameters appear in the dimensionless heat equation. We will see shortly why that provides a big advantage. Now we transform the boundary conditions. These are given in the problem statement as follows

$$\begin{aligned} T(x, t) &= T_0 & \text{at} & \quad t = 0 & \quad -b < x < b \\ T(x, t) &= T_1 & \text{at} & \quad t > 0 & \quad x = \pm b \end{aligned}$$

We substitute the dimensionless temperature and position variables into these statements to obtain

$$\begin{aligned} (T_1 - T_0)\Theta(\xi, \tau) + T_0 &= T_0 & \text{at} & \quad \tau = 0 & \quad -1 < \xi < 1 \\ (T_1 - T_0)\Theta(\xi, \tau) + T_0 &= T_1 & \text{at} & \quad \tau > 0 & \quad \xi = \pm 1 \end{aligned}$$

Simplifying these relations give

$$\begin{aligned} \Theta(\xi, \tau) &= 0 & \text{at} & \quad \tau = 0 & \quad -1 < \xi < 1 \\ \Theta(\xi, \tau) &= 1 & \text{at} & \quad \tau > 0 & \quad \xi = \pm 1 \end{aligned}$$

Notice the boundary conditions also contain no physical parameters. In summary, the complete model in dimensionless variables is given by

$\begin{aligned} \frac{\partial \Theta}{\partial \tau} &= \frac{\partial^2 \Theta}{\partial \xi^2} \\ \Theta(\xi, \tau) &= 0 & \text{at} & \quad \tau = 0 & \quad -1 < \xi < 1 \\ \Theta(\xi, \tau) &= 1 & \text{at} & \quad \tau > 0 & \quad \xi = \pm 1 \end{aligned}$
--

When we solve this equation *once*, we have solved the problem for *all parameter values*:  $k, \rho, \hat{C}_P, T_0, T_1, b$ . That provides a tremendous savings. □

### Example 2: Heating of a finite slab<sup>1</sup>

A solid slab of width  $2b$  is initially at temperature  $T_0$ . At time  $t = 0$ , the surfaces at  $x = \pm b$  are suddenly raised to temperature  $T_1$  and maintained at that temperature. Find  $T(x, t)$ .

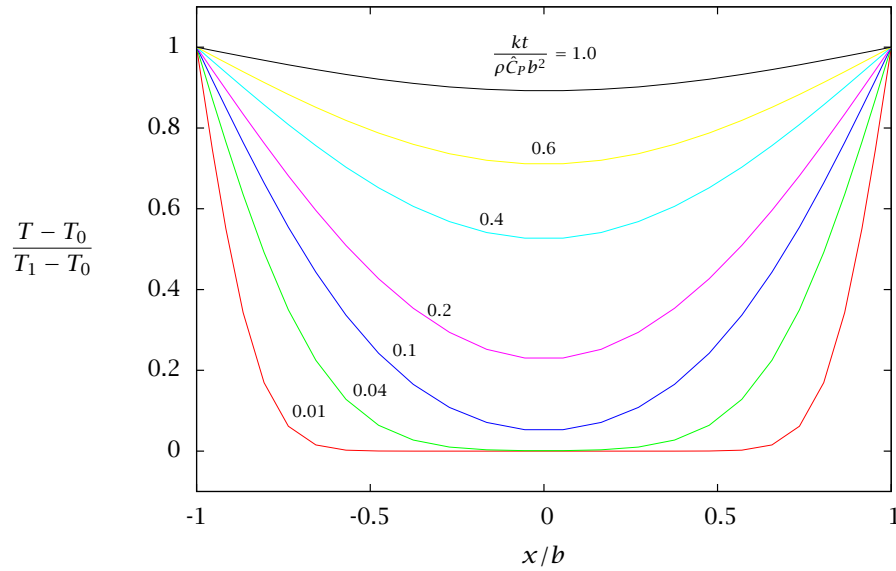


Figure 2: Temperature profile at several times during heating of a slab; various  $kt/(\rho\hat{C}_P b^2)$ .

### Solution

Dimensionless variables.

$$\theta = \frac{T - T_0}{T_1 - T_0} \quad \xi = \frac{x}{b} \quad \tau = \frac{kt}{\rho\hat{C}_P b^2}$$

Partial differential equation:

$$\frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial \xi^2}$$

Initial condition:

$$\text{at } \tau = 0, \quad \theta = 0 \quad \text{for } -1 < \xi < 1$$

Boundary condition:

$$\text{at } \xi = \pm 1, \quad \theta = 1 \quad \text{for } \tau > 0$$

Figure 2 shows the temperature profile at various times. □

<sup>1</sup>See also Bird et al. (2002, Example 12.1-2)

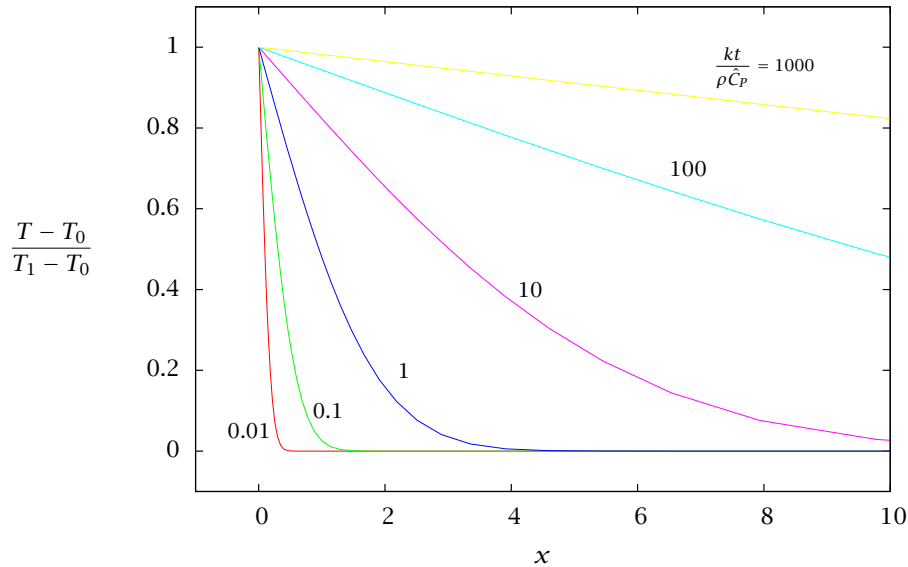


Figure 3: Temperature profile of the semi-infinite slab at different  $\tau = kt/(\rho\hat{C}_p)$ .

### Example 3: Heating of a semi-infinite slab<sup>2</sup>

A semi-infinite solid slab is initially at temperature  $T_0$ . At time  $t = 0$ , the surface at  $x = 0$  is suddenly raised to temperature  $T_1$  and maintained at that temperature. Find  $T(x, t)$ .

#### Solution

Define dimensionless temperature  $\Theta = (T - T_0)/(T_1 - T_0)$  and new time variable  $\tau = kt/(\rho\hat{C}_p)$ , which has units of  $(\text{length})^2$ . Notice we cannot make length dimensionless because we have no length scale in a semi-infinite solid.

Partial differential equation:

$$\frac{\partial \Theta}{\partial \tau} = \frac{\partial^2 \Theta}{\partial x^2}$$

Initial condition:

$$\text{at } \tau = 0, \quad \Theta = 0 \quad \text{for } 0 < x < \infty$$

Boundary condition:

$$\text{at } x = 0, \quad \Theta = 1 \quad \text{for } \tau > 0$$

<sup>2</sup>See also Bird et al. (2002, Example 12.1-1)

Change of variable that maps  $x \in (0, \infty)$  to  $z \in (0, 1)$

$$z = \frac{x}{x+1} \quad x = \frac{z}{1-z}$$

$$z_x = \frac{1}{(1+x)^2}$$

$$z_x = (1-z)^2$$

Chain rule once

$$\Theta(x, t) = \Theta(x(z), t) = \tilde{\Theta}(z, t)$$

$$\Theta_x = \tilde{\Theta}_z z_x$$

$$\Theta_x = \tilde{\Theta}_z (1-z)^2$$

Chain rule again

$$\Theta_{xx} = \left( \tilde{\Theta}_{zz} (1-z)^2 - 2(1-z)\tilde{\Theta}_z \right) (1-z)^2$$

$$\Theta_{xx} = \left( \tilde{\Theta}_{zz} (1-z) - 2\tilde{\Theta}_z \right) (1-z)^3$$

Transformed partial differential equation

$$\tilde{\Theta}_t = \left( \tilde{\Theta}_{zz} (1-z) - 2\tilde{\Theta}_z \right) (1-z)^3$$

with boundary conditions

$$\tilde{\Theta}(z, 0) = 0 \quad 0 < z < 1$$

$$\tilde{\Theta}(0, \tau) = 1 \quad \tau > 0$$

Notice there is only a single boundary condition at  $z = 0$  for a semi-infinite slab.

Figure 3 shows the temperature profile at various times. □

**Heat transfer coefficient.** If we imagine immersing a spherical body at a uniform temperature into a fluid held at a hotter temperature, we require the temperature of the sphere's outer surface to calculate the temperature profile. In Examples 2 and 3 we solved for the temperature profile under the assumption that the outer temperature jumped instantaneously from its initial temperature to the fluid temperature at  $t = 0$ . But this assumption is rather crude and empirical observations show that the body's outer temperature increases smoothly and does not jump instantly to the fluid's temperature. A more realistic way to model the outer temperature is through the use of a heat transfer coefficient,  $h$ . Empirical observations generally show that the heat flux is proportional to the temperature driving force between the bulk fluid temperature and the body's outer temperature. We define the



heat transfer coefficient to be this proportionality constant between temperature driving force and flux

$$q|_{r=R} = -k \left. \frac{\partial T}{\partial r} \right|_{r=R} = -h(T_b - T|_{r=R}) \quad (5)$$

in which  $T_b$  is the fluid temperature and  $T|_{r=R}$  is the spherical body's outer temperature. This empirical relationship is also known as Newton's law of cooling (Bird et al., 2002, p. 322). This relationship serves as the boundary condition on the body's exterior surface. Notice this boundary condition is a relationship between the temperature and temperature gradient at the outer surface of the body and the temperature of the bulk fluid.

We can nondimensionalize this boundary condition as well. In spherical coordinates we can define dimensionless variables as follows

$$\Theta = \frac{T - T_0}{T_b - T_0} \quad \xi = \frac{r}{R}$$

Notice we now use the fluid bulk temperature  $T_b$  in place of the body's outer temperature because the bulk temperature is constant, but the body's outer temperature is now changing with time given the new boundary conditions. Substituting these relations into Equation 5 gives

$$-k \left( \frac{T_b - T_0}{R} \right) \left. \frac{\partial \Theta}{\partial \xi} \right|_{\xi=1} = -h((T_b - T_0) - ((T|_{r=R} - T_0)))$$

in which we have added and subtracted  $T_0$  from the right-hand side. Rearranging this equation gives

$$\left. \frac{\partial \Theta}{\partial \xi} \right|_{\xi=1} = \left( \frac{hR}{k} \right) (1 - \Theta(1, t)) \quad \text{heat transfer boundary condition} \quad (6)$$

Notice the group  $hR/k$  is a dimensionless heat transfer coefficient. The dimensionless heat transfer coefficient is also known as the Nusselt number (Bird et al., 2002, p. 322).

$$\left. \frac{\partial \Theta}{\partial \xi} \right|_{\xi=1} = \text{Nu}(1 - \Theta(1, t))$$

in which

$$\text{Nu} = \left( \frac{hR}{k} \right) \quad \text{Nusselt number}$$

## 2 Mass diffusion

### 3 The Collocation Method for solving PDEs

In the collocation method, we approximate a function by passing a polynomial through values of the function at selected points. The selected points are known as collocation points. The locations of the collocation points have a large impact on how well the method

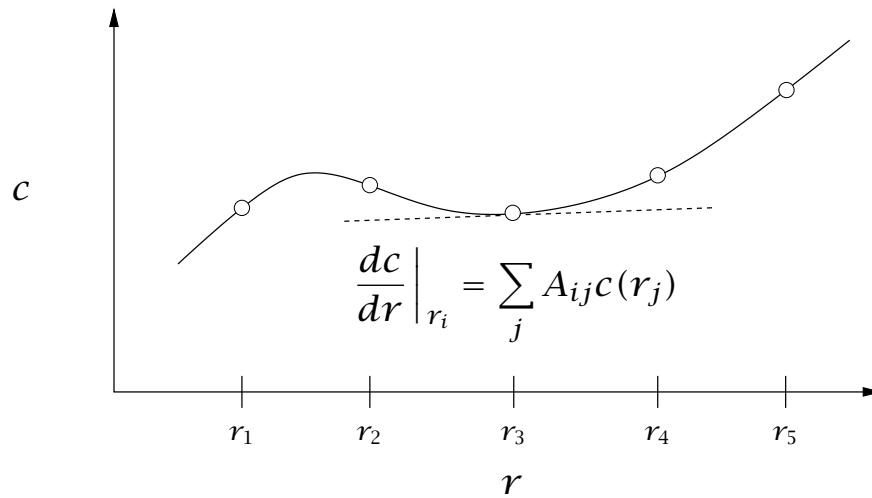


Figure 4: Function  $c(r)$  and its values at five collocation points,  $n_c = 5$ . Derivatives and integrals of the polynomial interpolant are linear combinations of the function values at the points.

works. Evenly spaced points, which seems a natural first choice, turns out to have mediocre properties. Choosing the points as zeros of a member of a family of orthogonal polynomials turns out to have much better properties. This choice is referred to as orthogonal collocation.

Figure 4 shows values of a function  $c(r)$  at five collocation points. The function is approximated by passing a polynomial through these points. To solve differential equations and boundary-value problems (BVP), we first compute the required derivatives of the polynomial approximation. We then find the values of the function such that the differential equation is satisfied at the collocation points. If we increase the number of collocation points,  $n_c$ , we require the differential equation to be satisfied at more locations, and we obtain a more accurate solution.

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

$$\begin{aligned} \left. \frac{dc}{dr} \right|_{r_i} &= \sum_{j=1}^{n_c} A_{ij} c(r_j) \\ \left. \frac{d^2c}{dr^2} \right|_{r_i} &= \sum_{j=1}^{n_c} B_{ij} c(r_j) \\ \int_0^1 f(r) dr &= \sum_{j=1}^{n_c} Q_j f(r_j) \end{aligned}$$

To obtain the locations of the collocation points and derivatives and integral weighting matrices and vectors, we use the function `colloc`, based on the methods described by Villadsen and Michelsen (1978).

```
[R A B Q] = colloc(npts-2, 'left', 'right');
```

The strings 'left' and 'right' specify that we would like to have collocation points at the endpoints of the interval in addition to the zeros of the orthogonal polynomial. We solve for the concentration profile for the reaction-diffusion problem in a catalyst pellet to illustrate the collocation method.

#### Example 4: Single-pellet profile

Consider the isothermal, first-order reaction-diffusion problem in a spherical pellet

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) - \Phi^2 c = 0 \quad (7)$$

$$c = 1, \quad r = 3$$

$$\frac{dc}{dr} = 0, \quad r = 0$$

The effectiveness factor is given by

$$\eta = \frac{1}{\Phi^2} \frac{dc}{dr} \Big|_{r=3}$$

1. Compute the concentration profile for a first-order reaction in a spherical pellet. Solve the problem for  $\phi = 10$ .
2. Plot the concentration profile for  $n_c = 5, 10, 30$  and  $50$ . How many collocation points are required to reach accuracy in the concentration profile for this value of  $\Phi$ .
3. How many collocation points are required to achieve a relative error in the effectiveness factor of less than  $10^{-5}$ ?

#### Solution

First we perform the differentiation in Equation 7 to obtain

$$\frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} - \Phi^2 c = 0$$

We define the following Octave function to evaluate this equation at the interior collocation points. At the two collocation endpoints, we satisfy the boundary conditions  $dc/dr = 0$  at  $r = 0$  and  $c = 1$  at  $r = 3$ . The function is therefore

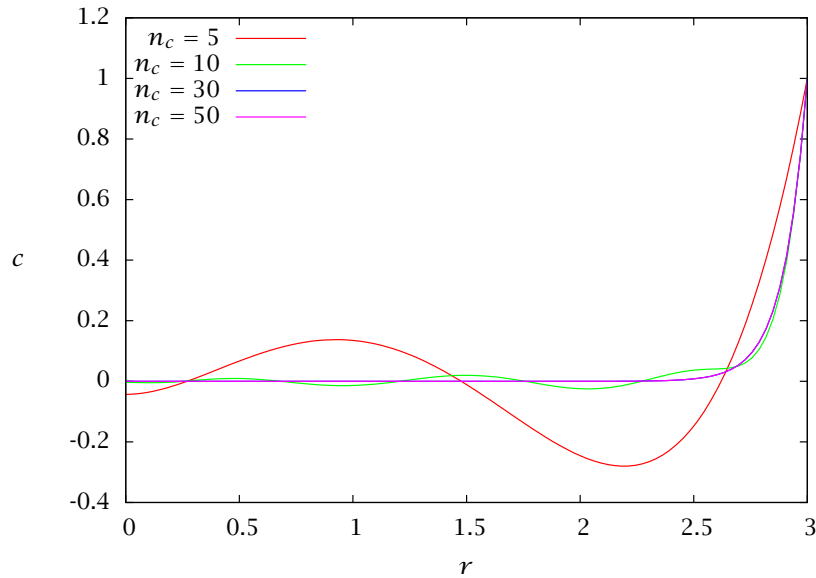


Figure 5: Dimensionless concentration versus dimensionless radial position for different numbers of collocation points.

```
function retval = pellet(c)
    global Phi A B R n
    %% differential equation at col pts
    retval = B*c .+ 2*A*c./R .- Phi^2*c;
    %% overwrite ends with boundary conditions
    retval(1) = A(1,:)*c;
    retval(n) = 1 - c(n);
```

Figure 5 shows the concentration profiles for different numbers of collocation points. We require about  $n_c = 30$  to obtain a converged concentration profile. Figure 6 shows the relative error in the effectiveness factor versus number of collocation points. If one is only interested in the pellet reaction rate, about 16 collocation points are required to achieve a relative error of less than  $10^{-6}$ .  $\square$

#### 4 Implicit Differential Equations and Differential-Algebraic Equations

Some models require a more general structure than the ODE,

$$d\mathbf{x}/dt = \mathbf{f}(\mathbf{x}, t)$$

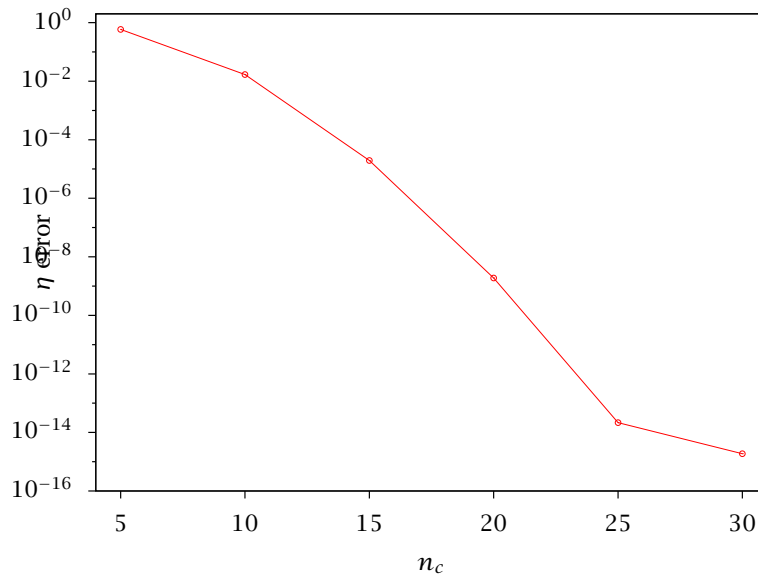


Figure 6: Relative error in the effectiveness factor versus number of collocation points.

Often we have combinations of differential and algebraic equations, known as differential-algebraic equations (DAEs). To address these models, consider the more general form of implicit ODEs

$$\mathbf{0} = \mathbf{f}(d\mathbf{x}/dt, \mathbf{x}, t)$$

Both DAEs and ODEs can be considered special cases of this structure. Brenan et al. Brenan, Campbell, and Petzold (1989) provide further reading on existence and uniqueness of solutions to these models, which are considerably more complex issues than in the case of simple ODEs. Initial conditions are required for  $d\mathbf{x}/dt$  as well as  $\mathbf{x}$  in this model,

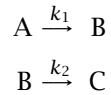
$$\frac{d\mathbf{x}}{dt}(t) = \dot{\mathbf{x}}_0 \quad \mathbf{x}(t) = \mathbf{x}_0, \quad \text{at } t = 0$$

Petzold has provided a numerical package, `dassl`, to compute solutions to implicit differential, and differential-algebraic equations. The main difference between using `dassl` and `lsode` is the form of the user-supplied function defining the model. A second difference is that the user must supply  $\dot{\mathbf{x}}_0$  as well as  $\mathbf{x}_0$ .

In MATLAB, the program `ode15i` solves implicit differential equations. The following example shows how to use `ode15i` to solve implicit differential equations, in this case differential-algebraic equations.

**Example 5: Quasi-steady state assumption gives rise to DAEs**

Consider the following simple series reactions



The full set of differential equations for a well-mixed reactor are

$$\begin{aligned} \frac{dc_A}{dt} &= -r_1 &&= -k_1 c_A \\ \frac{dc_B}{dt} &= r_1 - r_2 &&= k_1 c_A - k_2 c_B \\ \frac{dc_C}{dt} &= r_2 &&= k_2 c_B \end{aligned}$$

When the rate constants for production of a species are small compared to the rate constants for its removal, we can reduce the model using what is known as the quasi-steady-state assumption. In this example let's assume that  $k_1 \ll k_2$ , so species B is a highly reactive intermediate. Then, instead of solving B's differential equation, we wish to simplify the model by assuming the B concentration equilibrates *immediately* to its steady-state value given by setting its time derivative to zero or

$$k_1 c_A - k_2 c_B = 0$$

We replace the *differential equation for B* with this *algebraic constraint*. So for the reduced model, we solve the DAE model

$$\begin{aligned} \frac{dc_A}{dt} &= -r_1 &&= -k_1 c_A \\ 0 &= r_1 - r_2 &&= k_1 c_A - k_2 c_B \\ \frac{dc_C}{dt} &= r_2 &&= k_2 c_B \end{aligned}$$

The QSSA reduced model consists of two differential equations and one algebraic equation instead of the full model's three differential equations.

- (a) Solve the full model and plot  $c_A, c_B, c_C$  versus time using for the following parameters

$$k_1 = 1 \quad k_2 = 10 \quad c_{A0} = 1 \quad c_{B0} = 0 \quad c_{C0} = 0$$

- (b) Solve the QSSA reduced model for the same parameter values. Note however that you need to find a value of  $c_{B0}$  that is consistent with the algebraic equation at  $t = 0$  or the DAE solver may fail.

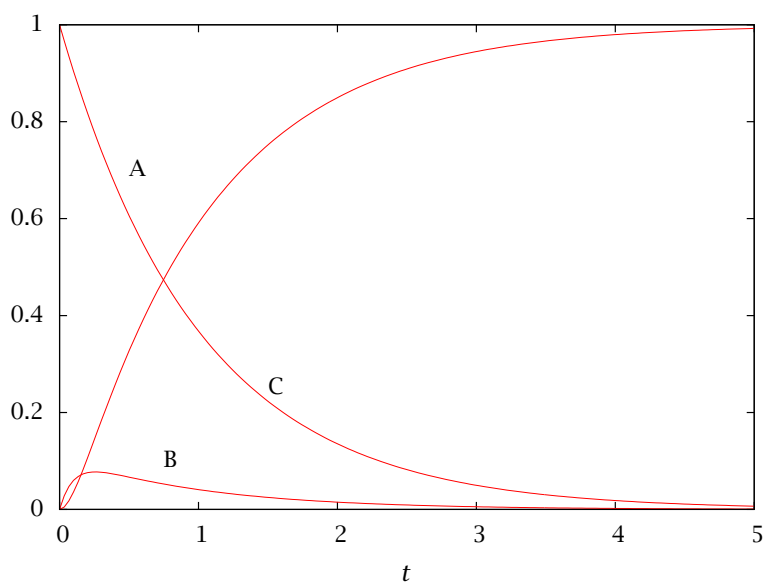


Figure 7: The solution to the full model for the series reaction  $A \rightarrow B \rightarrow C$ ; ODE model.

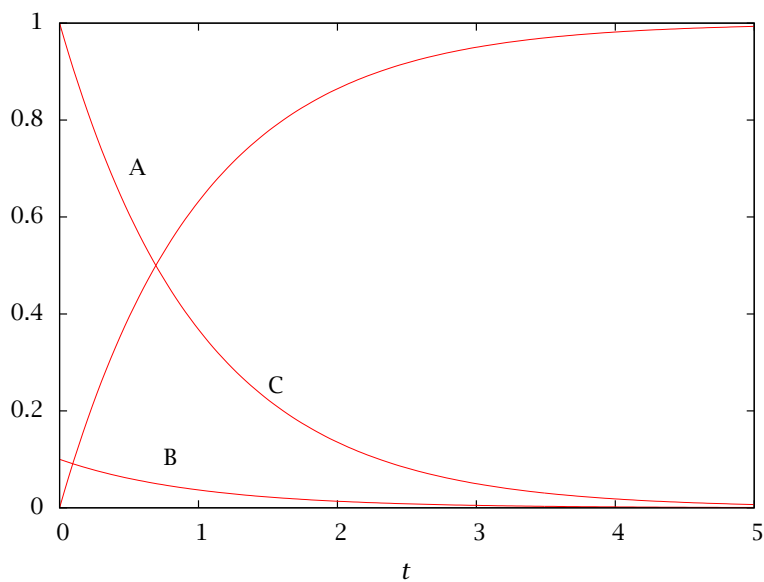


Figure 8: The solution to the reduced QSSA model; DAE model.

**Solution**

- (a) Figure 7 shows the solution to the full model. We use the following call to the ODE solver `ode15s` and the following function `rates` to evaluate the differential equations.

```
function dcdt = rates(t, x)
    global k1 k2
    ca = x(1); cb = x(2); cc = x(3);
    r1 = k1*ca; r2 = k2*cb;
    dcdt = [-r1; r1-r2; r2];
```

```
[tout, x] = ode15s (@rates, time, x0, opts);
```

- (b) Figure 8 shows the solution to the QSSA model. Notice that the intermediate B is highly reactive and present only in small concentration compared to the reactant A and main product C. Also, we see that the full model with three ODEs shows the rapid approach of species B to its quasi-steady-state value. Using the reduced QSSA model removes this transient and species B jumps instantly to its quasi-steady-state value. The small difference in B's dynamics has no noticeable impact on the behavior of A and C. For these rate constant values ( $k_1 = 1, k_2 = 10, k_1 \ll k_2$ ), the QSSA provides an accurate reduced model.

We use the following call to the DAE solver `ode15i` and the following function `qssa` to evaluate the residuals of the DAEs. Notice the similarities and differences between the functions `qssa` and `rates`.

```
function resid = qssa(t, x, xdot)
    global k1 k2
    ca = x(1); cb = x(2); cc=x(3);
    cadot = xdot(1); cbdot = xdot(2); ccdot = xdot(3);
    r1 = k1*ca; r2 = k2*cb;
    resid = [-cadot - r1; r1 - r2; -ccdod + r2];
end
```

```
[tout, x] = ode15i (@qssa, time, x0, xdot0, opts);
```

□



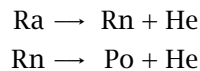
## 5 Automatic Stopping Times for Differential Equations

We often wish to stop ODE solvers when certain conditions are met. Two examples are when we have reached a certain conversion, and when we have created a new phase and need to change the ODEs governing the system.

In MATLAB we tell the ODE solver to terminate the integration by setting the 'Events' flag as follows. Recall we *always* tighten the default ODE solver error tolerances as well. We can do both in one call to `opts`

```
tol = sqrt(eps);
opts = odeset ('Events', @stoptime, 'AbsTol', tol, 'RelTol', tol);
```

The user then provides a function `stoptime` and the ODE solver stops when this function reaches zero. Consider Example 1 of the “Chemical kinetics in well-mixed reactors” module. Figure 5 of that module shows the mass of Ra, Rn, He, and Po versus time for the kinetic mechanism



Say we want the ODE solver to find the time at which Ra reaches a given value. If Ra is the first value in the  $x$  vector of differential equations, then the `stoptime` function is

```
function [fcnval, isterm, dir] = stoptime(t, x)
    global Ravalue
    fcnval = x(1) - Ravalue;
    isterm = 1;
    dir = 0;
```

The time at which this function reaches zero is then reported back by `ode15s` in the last value of vector `tout`

```
[tout, x] = ode15s (@rates, time, x0, opts);
```

Notice that if the event is detected during the ODE solution, then the vector of solution times `tout` returned by the ODE solver is *different* than the user-requested vector of solution times `time`. The `tout` vector is a truncated version of `time` with the event time as the final value in the vector. Try the command `doc odeset` at the MATLAB command line if you require more information about setting the 'Events' flag.

## 6 Exercises

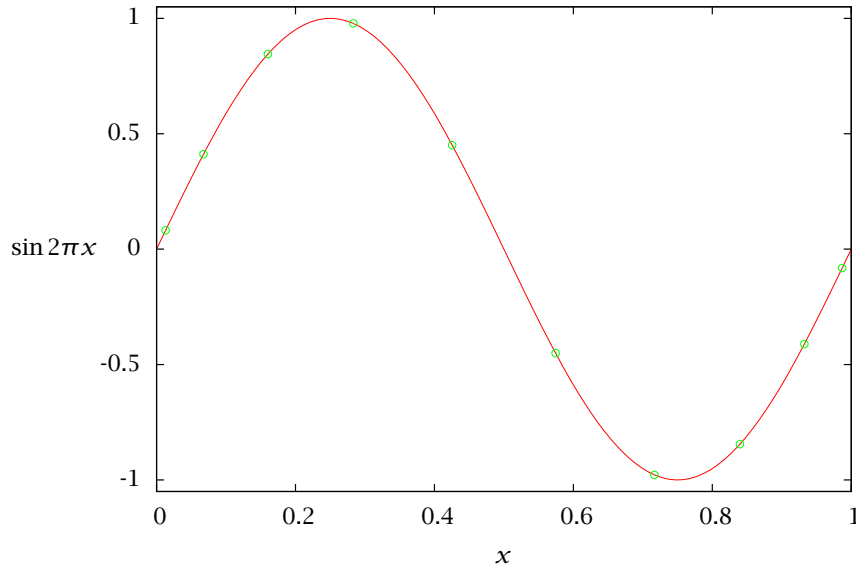


Figure 9: The function  $\sin 2\pi x$  and 10 collocation points.

### Exercise 1: Checking the derivative formulas. Oscillating function

Consider the following function on the interval  $0 \leq x \leq 1$

$$y(x) = \sin 2\pi x$$

Note that as shown in Figure 9 this function does not resemble a polynomial.

So let's examine how accurately the polynomial collocation procedure can evaluate the first and second derivatives. Choose  $n = 10$  collocation points on the  $x$  interval.

- Evaluate the collocation approximation  $Y_i = y(x_i)$ , at the  $n$   $x_i$  collocation points. Plot  $y(x)$  and  $Y_i$  versus  $x$ . You should obtain a plot similar to Figure 9.
- Next differentiate the function  $y(x)$  and plot the analytical result versus  $AY$  at the collocation points. Compute the relative errors at the collocation points and plot this result.
- Next take the second derivatives of the function  $y(x)$  and plot the analytical result versus  $BY$  at the collocation points. Compute the relative errors at the collocation points and plot this result.
- Repeat these steps for  $n = 20$  collocation points.

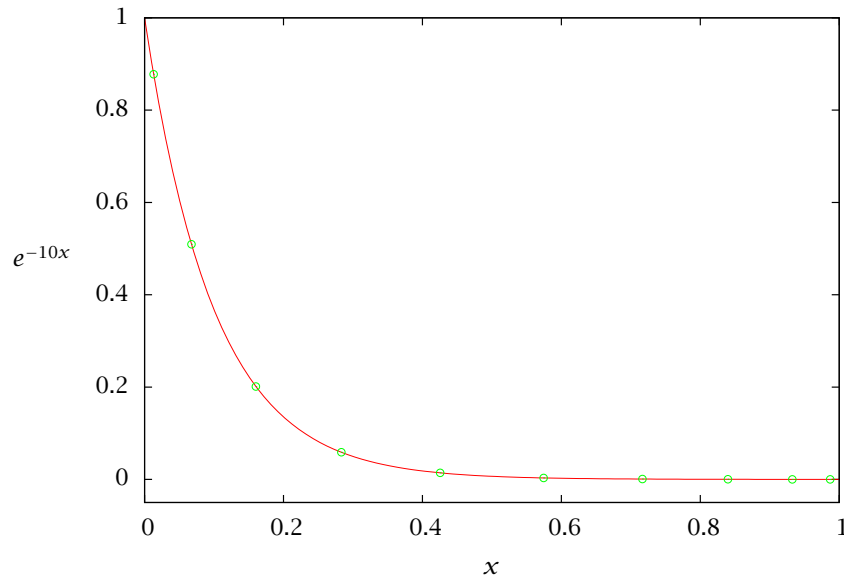


Figure 10: The function  $e^{-10x}$  and 10 collocation points.

### Exercise 2: Checking the derivative formulas. Exponential function

Repeat Exercise 1 but use the function

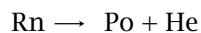
$$z(x) = e^{-10x}$$

shown in Figure 10. Notice this function also does not resemble a polynomial.

Which function appears to be more difficult to approximate with polynomials,  $\sin 2\pi x$  or  $e^{-10x}$ ? Why?

### Exercise 3: Stopping conditions for radioactive decay reactions

Consider again the two radioactive decay reactions of Example 1 of the “Chemical kinetics in well-mixed reactors” module.



- Use an ODE solver to find the time at which the Ra mass reaches half of its initial value. Plot Ra, Rn, He, Po versus time up to this time.
- Compare the value reported by the ODE solver to the half life given in the problem. What is the relative error in the ODE solver's value? If you wanted more accuracy in the ODE solver's reported time, how would you obtain it?

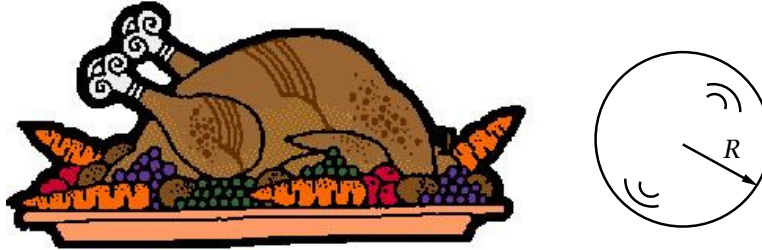


Figure 11: Model the stuffed turkey as a sphere filled with water.

#### Exercise 4: Heat equation with an insulated end

Consider again the heating of the slab as in Example 2, but replace the boundary condition at  $x = -b$  with an insulated boundary. An insulated boundary does not allow any heat flux so we have

$$q = k \frac{\partial T}{\partial x} = 0$$

- Replace the boundary condition  $T = T_1$  at  $x = -b$  with this zero derivative condition and resolve the problem. Note you will require a DAE solver for this problem. Plot the temperature profile versus time at the same times as shown in Example 2.
- Does the slab heat up more quickly or more slowly with the insulated end. Explain why.

#### Exercise 5: Cooking the turkey<sup>3</sup>

For heat transfer and cooking purposes, consider modeling a stuffed turkey as a sphere filled with water as depicted in Figure 11. The oven is set at 325°F. Assume the turkey's outer temperature is 50°F lower than the oven temperature. The turkey is finished cooking when the center temperature reaches 180°F.

- Write out the dimensionless heat equation in spherical coordinates starting with the dimensional heat equation in spherical coordinates

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 k \frac{\partial T}{\partial r} \right) \quad (8)$$

Convenient dimensionless variables are

$$\Theta = \frac{T - T_0}{T_1 - T_0} \quad \xi = \frac{r}{R} \quad \tau = \frac{kt}{\rho \hat{C}_p R^2}$$

<sup>3</sup>See also Bird et al. (2002, Problem 12B.7)

in which  $T_0$  is room temperature,  $T_1$  is the turkey's outer temperature during cooking, and  $R$  is the sphere radius.

What is the dimensionless center temperature when the turkey is finished cooking?

- (b) Solve the dimensionless heat equation with a stopping condition to find the time when the center temperature reaches the value found in the previous part. Note you will require a DAE solver for this problem.

What is the dimensionless stopping time when the turkey is finished cooking?

Plot the temperature profile in the sphere at this dimensionless stopping time?

- (c) Prepare a cooking time versus turkey weight chart over the turkey weight range 10 to 25 pounds. How many times must you solve the heat equation to prepare this plot?

### Exercise 6: Turkey with increased heat transfer resistance

Resolve Exercise 5 assuming that the outer turkey temperature is 75°F lower than the oven temperature.

### Exercise 7: Using a heat transfer coefficient

Consider using the heat transfer coefficient to model the outer boundary of the sphere in Exercise 5.

- (a) Solve the dimensionless version of Equation 8 with the boundary condition given in Equation 6. Prepare the cooking chart for the following dimensionless heat transfer coefficient

$$\frac{hR}{k} = 3$$

Does the cooking time increase or decrease compared to the chart in Exercise 5?

- (b) Plot the sphere's outer temperature versus time.

- (c) Repeat the calculations for

$$\frac{hR}{k} = 5$$

### Exercise 8: Cooling off the beer

Winter has returned to Madison. You've invited friends over for one last party before exams, and are almost done setting up when suddenly you realize that the beer is still sitting in your closet at room temperature. You need to chill it quickly, and so decide to fill your bathtub with ice water and throw the drinks in there to speed up the cooling process. Your roommate suggests putting the beer outside on the balcony instead. Since your roommate is a philosophy major, you naturally question his judgment. "Look," you tell him, "the



Figure 12: Model the beer can as a cylinder filled with water.

surrounding water in the tub gives a way better heat transfer coefficient than air. The Nusselt number's enormous! The bathtub is the way to go."

"Well, I don't know what a Nusselt is," your roommate replies, "but it's zero degrees outside! The balcony's going to be faster for sure." Exasperated, you say, "OK, Plato, why don't you work out whether or not the beer exists and let me take care of the cooling, alright? I've taken CBE 255; I know what I'm doing."

Solve the heat transfer equation for these two situations. To simplify the problem let's model the can of beer as a semi-infinite cylinder as depicted in Figure 12. The heat equation for this geometry is

$$\rho \hat{C}_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r k \frac{\partial T}{\partial r} \right) \quad (9)$$

Model the heat transfer as pure heat conduction and ignore any fluid motions that might take place inside the can during the cooling process.

- (a) Write down the dimensionless heat equation for this problem. So we are all consistent, define the dimensionless temperature as

$$\Theta = \frac{T - T_b}{T_0 - T_b}$$

in which  $T_0$  is the initial temperature and  $T_b$  is the fluid temperature in which the cylinder is immersed. What do you use for dimensionless time  $\tau$  and radius,  $\xi$ ?

- (b) Show that the initial condition is  $\Theta(\xi, 0) = 1$  for both the bathtub and the balcony.

Show that the outer boundary condition is

$$\frac{\partial \Theta}{\partial \xi} = -\text{Nu} \Theta \quad \tau > 0 \quad \xi = 1$$

What is your definition of Nu?

What is the second boundary condition?

- (c) Find the final time (in minutes) for the center of the cylinder to reach 45°F for both cases. Your guests are arriving in 45 minutes. Are you going to make it?

Here are the rest of the data

$$\begin{aligned} T_{\text{balcony}} &= 0^\circ\text{F} & \text{Nu}_{\text{balcony}} &= 0.8 \\ T_{\text{bathtub}} &= 32^\circ\text{F} & \text{Nu}_{\text{bathtub}} &= 8 \\ R &= 3 \text{ cm} \end{aligned}$$

- (d) Plot the transient can temperature profiles for both cases on separate plots.

### Exercise 9: Using MATLAB's pdepe to solve PDEs

Solve Example 2 using pdepe and produce a new version of Figure 2. Compare to the version given in the module.

### Exercise 10: More pdepe

Solve Exercise 4 using pdepe. (Ignore the remark about a DAE solver.)

### Exercise 11: One more pdepe

Consider again Example 2, but modify the problem such that the boundary conditions on both surfaces of the slab involve a heat transfer coefficient characterized by a Nusselt number equal to 2.

Solve the modified problem using pdepe. Generate a plot of the solution of the same form as Figure 2 and compare.

### Exercise 12: Carbon dioxide adsorption in a zeolite bed

The following isotherm equation has been fitted to data for adsorption of CO<sub>2</sub> on zeolite 5A adsorbent at 50°C:

$$w = \frac{w_{\text{max}}(KP)^b}{1 + (KP)^b}$$

Here,  $w$  denotes mass of CO<sub>2</sub> adsorbed per mass of adsorbent in equilibrium at a CO<sub>2</sub> partial pressure of  $P$ . Parameters  $w_{\text{max}} = 0.2079$ ,  $K = 9.6409 \text{ bar}^{-1}$ , and  $b = 0.7488$ .

A mixture of CO<sub>2</sub> and inert gas is passed through a bed of this adsorbent. The bed initially contains a low CO<sub>2</sub> loading of  $w = 0.0001$  throughout the bed. The CO<sub>2</sub> partial pressure in the inlet gas is approximately 0.0937 bar, which corresponds to a value of  $w_{\text{in}} = 0.10$  in equilibrium with the adsorbent. The inlet gas temperature is 50°C. In the following it will be assumed that the bed temperature is controlled and remains constant at 50°C.

The behavior of the bed is modeled by the following PDE.

$$\frac{\partial w}{\partial t} = -\left(\frac{M}{\rho_s A}\right) \frac{\partial \dot{n}_A}{\partial x} + D \frac{\partial^2 w}{\partial x^2}$$

$x$  is the distance along the bed from the feed end and  $t$  is time.  $M = 44.01$  kg/kmol is the molecular weight of  $\text{CO}_2$ ,  $\rho_s = 700$  kg/m<sup>3</sup> is the bulk density of the adsorbent packed in the bed, and  $A = 1.0 \times 10^{-3}$  m<sup>2</sup> is the cross-sectional area of the bed. The length of the bed  $L = 1$  m. Constant  $D$  quantifies the amount of axial dispersion in the bed.

$\dot{n}_A$  is the molar flowrate of  $\text{CO}_2$  through the bed, which is related to the molar flowrate  $\dot{n}_I$  of the inert gas by

$$\dot{n}_A = \dot{n}_I \left( \frac{P}{P_{\text{tot}} - P} \right)$$

The total pressure of the gas flowing through the bed is approximately constant at  $P_{\text{tot}} = 1$  bar. By combining the above relation for  $\dot{n}_A$  with the isotherm, the governing PDE can be written

$$\frac{\partial w}{\partial t} = - \left( \frac{M}{\rho_s A} \right) \left( \frac{d\dot{n}_A}{dP} \right) \left( \frac{dw}{dP} \right)^{-1} \cdot \frac{\partial w}{\partial x} + D \frac{\partial^2 w}{\partial x^2}$$

If the isotherm is solved for  $P$  as a function of  $w$ , then the terms in parentheses can be computed as functions of  $w$ .

- Solve this PDE model using `pdepe`. Use the term described as “ $s(x, t, u, \frac{\partial u}{\partial x})$ ” in the MATLAB help to represent the term involving  $\frac{\partial w}{\partial x}$ . Set the term “ $f(x, t, u, \frac{\partial u}{\partial x})$ ” equal to  $D \cdot \frac{\partial^2 w}{\partial x^2}$  to represent the term involving  $\frac{\partial^2 w}{\partial x^2}$ .  
Run the model with a flowrate  $\dot{n}_I = 2.9 \times 10^{-3}$  kmol/min for a time duration of  $t_f = 5$  min. Set `xmesh` to get a grid of 101 points along the length of the bed, and set  $D = 0.003$ .
- Plot the solution time trajectories for all of the  $x$  mesh points using `plot(tspan, sol)`.
- Plot the time trajectories of  $w(x, t)$  for the five  $x$  values 0, 0.25, 0.5, 0.75, and 1.0.
- Plot the function  $w(x, t)$  for the 11 values of time ranging from  $t = 0$  to  $t = 5$  min in 0.5 min intervals.
- Compare the results obtained with  $D = 0.003$  with the results produced with  $D = 0.03$ .
- Repeat the above, changing the value of  $D$  to 0.001 and 0.0003.

### Exercise 13: Desorption of carbon dioxide

Consider again the  $\text{CO}_2$  adsorption bed model in Exercise 12 parts (a)–(d). After the adsorption process in part (a) is finished and the adsorbent is loaded with  $\text{CO}_2$ , the bed is regenerated by passing a  $\text{CO}_2$ -lean stream through the bed. Model the desorption process by setting the initial state of the bed equal to the final state that resulted at the end of the adsorption process. The  $\text{CO}_2$ -lean stream enters at  $x = 0$  with an inert gas flowrate  $\dot{n}_I = 2.9 \times 10^{-3}$  kmol/min and a  $\text{CO}_2$  partial pressure equivalent to an equilibrium adsorption level of  $w_{\text{lean}} = 0.02$ . Make a plot of the  $\text{CO}_2$  mole fraction in the exit gas stream versus time. Approximately how long does it take to desorb most of the  $\text{CO}_2$ ?



**References**

- R. B. Bird, W. E. Stewart, and E. N. Lightfoot. *Transport Phenomena*. John Wiley & Sons, New York, second edition, 2002.
- K. E. Brenan, S. L. Campbell, and L. R. Petzold. *Numerical Solution of Initial-Value Problems in Differential-Algebraic Equations*. Elsevier Science Publishers, New York, 1989.
- J. Villadsen and M. L. Michelsen. *Solution of Differential Equation Models by Polynomial Approximation*. Prentice-Hall, Englewood Cliffs New Jersey, 1978.