TMA225 Differential equations and scientific computing, part A

EXAMPLE PROBLEM: THE CATALYST PELLET

1. Introduction

A substance in gas form is diffusing into a porous catalyst pellet, where it reacts in a first order reaction under isothermal conditions. This leads to the reaction-diffusion equation,

$$\begin{aligned} \frac{\partial u}{\partial t} - \nabla \cdot \big(a \nabla u\big) + cu = 0, &\quad \text{in } \Omega, \\ u = g_D, &\quad \text{on } \partial\Omega, \end{aligned} \tag{1}$$

where u `[mol/m`^{3}`]` is the concentration of the interesting substance in the catalyst pellet, g_D is the (constant) ambient concentration, a `[m`^{2}`/s]` is the diffusion coefficient, c `[s`$^{-1}$`]` is the rate coefficient of the reaction, L `[m]` is the diameter of the pellet, and $\nabla u = (\frac{\partial u}{\partial x_1}, \frac{\partial u}{\partial x_2}, \frac{\partial u}{\partial x_3})$.

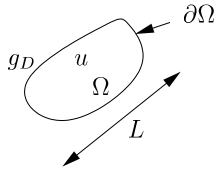

Figure 1. The catalyst pellet.

Note that we make the simplifying assumption that the temperature is constant. This assumption is the same as saying that we ignore the temperature dependence in the rate coefficient $c = c_0 \exp(-E/(RT))$ given by Arrhenius' law. However, we want to allow the diffusion and catalyzation properties to be different in different parts of the pellet. This means that a, c_0, and E may vary with position, so that $a = a(x_1, x_2, x_3)$, $c = c(x_1, x_2, x_3)$.

2. Dimensionless Variables

We now introduce *dimensionless variables.* Let $u_{\mathrm{ref}} = g_D$, a_{ref}, c_{ref}, $L_{\mathrm{ref}} = L$, be reference constants, and set

$$u^* = u/g_D, \quad a^* = a/a_{\mathrm{ref}}, \quad c^* = c/c_{\mathrm{ref}}, \quad (x_1^*, x_2^*, x_3^*) = (x_1/L, x_2/L, x_3/L).$$

By choosing the reference constants a_{ref} and c_{ref} such that they represent the typical order of magnitude of a and c, we may *scale* the variables so that they are neither very big nor very small, which is desirable from a numerical point of view. Note that, by the chain rule,

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$$\nabla u = (\frac{\partial u}{\partial x_1}, \frac{\partial u}{\partial x_2}, \frac{\partial u}{\partial x_3}) = (\frac{\partial (g_D u^*)}{\partial x_1^*}\frac{dx_1^*}{dx_1}, \frac{\partial (g_D u^*)}{\partial x_2^*}\frac{dx_2^*}{dx_2}, \frac{\partial (g_D u^*)}{\partial x_3^*}\frac{dx_3^*}{dx_3}) = \frac{g_D}{L}\nabla^* u^*,$$

where $\nabla^* = (\frac{\partial}{\partial x_1^*}, \frac{\partial}{\partial x_2^*}, \frac{\partial}{\partial x_3^*}) = (L\frac{\partial}{\partial x_1}, L\frac{\partial}{\partial x_2}, L\frac{\partial}{\partial x_3}) = L\,\nabla$. By using the chain rule again, we get,

$$\nabla \cdot \big(a \nabla u\big) = \frac{a_{\mathrm{ref}}\, g_D}{L^2}\, \nabla^* \cdot \big(a^* \nabla^* u^*\big),$$

and (1) thus becomes,

$$\begin{aligned} \frac{\partial u}{\partial t} - \frac{a_{\mathrm{ref}}\, g_D}{L^2}\, \nabla^* \cdot \big(a^* \nabla^* u^*\big) + c_{\mathrm{ref}}\, c^* g_D u^* &= 0, \quad \text{in } \Omega^*, \\ u^* &= 1, \quad \text{on } \partial\Omega^*, \end{aligned} \tag{2}$$

Dividing (2) by $\frac{a_{\mathrm{ref}}\, g_D}{L^2}$, we get,

$$\begin{aligned} \frac{L^2}{a_{\mathrm{ref}}}\frac{\partial (u/g_D)}{\partial t} - \nabla^* \cdot \big(a^* \nabla^* u^*\big) + \frac{L^2 c_{\mathrm{ref}}}{a_{\mathrm{ref}}}\, c^* u^* &= 0, \quad \text{in } \Omega^*, \\ u^* &= 1, \quad \text{on } \partial\Omega^*. \end{aligned} \tag{3}$$

Finally, introducing the dimensionless number $\phi = L\sqrt{c_{\mathrm{ref}}/a_{\mathrm{ref}}}$ (the *Thiele modulus*), and the *time scale*[1] $t_{\mathrm{ref}} = L^2/a_{\mathrm{ref}}$, we get

$$\begin{aligned} \frac{\partial u^*}{\partial t^*} - \nabla^* \cdot \big(a^* \nabla^* u^*\big) + \phi^2 c^* u^* &= 0, \quad \text{in } \Omega^*, \\ u^* &= 1, \quad \text{on } \partial\Omega^*, \end{aligned} \tag{4}$$

where $t^* = t/t_{\mathrm{ref}}$ is a dimensionless time variable, and we have again used the chain rule,

$$\frac{\partial u^*}{\partial t^*} = \frac{\partial (u/g_D)}{\partial t}\frac{dt}{dt^*} = t_{\mathrm{ref}}\frac{\partial (u/g_D)}{\partial t}.$$

If the diffusion and rate coefficients are constant, then, of course, we take $a_{\mathrm{ref}} = a$, $c_{\mathrm{ref}} = c$, so that $a^*(x_1^*, x_2^*, x_3^*) \equiv 1$, $c^*(x_1^*, x_2^*, x_3^*) \equiv 1$, and (4) becomes

$$\begin{aligned} \frac{\partial u^*}{\partial t^*} - \Delta^* u^* + \phi^2 u^* &= 0, \quad \text{in } \Omega^*, \\ u^* &= 1, \quad \text{on } \partial\Omega^*, \end{aligned} \tag{5}$$

where $\Delta^* = \frac{\partial^2}{\partial x_1^{*2}} + \frac{\partial^2}{\partial x_2^{*2}} + \frac{\partial^2}{\partial x_3^{*2}}$ is the Laplace operator.

[1] This is a natural time scale for the problem, depending on the relation between the size of the pellet and the "speed" of the diffusive transport.

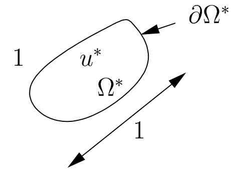

FIGURE 2. The pellet in dimensionless variables.

We here give some reasons for writing the mathematical model in dimensionless form, including the one already mentioned:

- the dimensionless equation (5) contains fewer constants and variables than the original equation and is therefore more convenient to work with;
- it gives a possibility of scaling the variables so that they are neither very big nor very small;
- it is useful for scaling an apparatus from laboratory size to factory size; this should be done so that the dimensionless constants are the same;
- in a sense, we need not bother to find realistic values for the physical parameters a, c_0, E; since they are conveniently grouped into the dimensionless number ϕ, we can just say that we want to solve the equation for small, medium and large values of ϕ.

3. Effectiveness Factor

We now consider the *stationary case*, i.e., we assume that the system has reached a stationary state. In this case, the reaction-diffusion equation (4) reads,

$$\begin{aligned} -\nabla^* \cdot \big(a^* \nabla^* u^*\big) + \phi^2 c^* u^* &= 0, \quad \text{in } \Omega^*, \\ u^* &= 1, \quad \text{on } \partial\Omega^*. \end{aligned} \tag{6}$$

The concentration, and hence the reaction rate, will be lower in the middle of the pellet. This means that the catalyzing power of the pellet is not fully used. The efficiency of the catalyst pellet is measured by the quotient of the *actual* total reaction rate and the *ideal* reaction rate that would be achieved if the concentration and the rate coefficient were everywhere equal to the their reference values, i.e., if $u = g_D$, $c = c_{\text{ref}}$. This quotient is called the *effectiveness factor* and is given by

$$\eta = \frac{\iiint_\Omega cu \, dx_1 dx_2 dx_3}{c_{\text{ref}} \, g_D |\Omega|} = \frac{1}{|\Omega^*|} \iiint_{\Omega^*} c^* u^* \, dx_1^* dx_2^* dx_3^*, \tag{7}$$

where $|\Omega|$ and $|\Omega^*|$ denotes the *volume* of Ω and Ω^* respectively. Show this equality!

Exercise 1. Show that η can also be expressed in terms of the flux through the boundary of the pellet: (n^* is the exterior unit normal vector)

$$\eta = \frac{1}{\phi^2} \frac{1}{|\Omega^*|} \iint_{\partial\Omega^*} n^* \cdot (a^* \nabla^* u^*) \, dS^*. \tag{8}$$

Hint: use (6) and Gauss' divergence theorem.

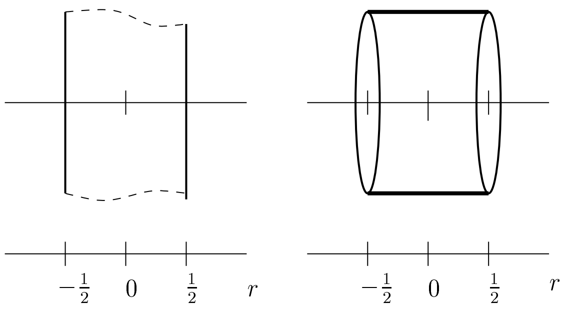

FIGURE 3. Slab and cylinder.

4. An exact solution

If the coefficients are constant and the geometry of the pellet is simple, namely, a slab, a circular cylinder, or a sphere, then we can solve (6) analytically. We study one of these examples here.

Exercise 2. If the pellet is a slab (or a cylinder with sealed mantle surface), Figure 3, then u^* depends only on the axial coordinate $r = x_1^* = x_1/L$ and (5) (in the stationary case) becomes,

$$\begin{aligned} -\frac{d^2u^*}{dr^2} + \phi^2 u^* = 0, \quad -\tfrac{1}{2} < r < \tfrac{1}{2}, \\ u^*(-\tfrac{1}{2}) = u^*(\tfrac{1}{2}) = 1. \end{aligned} \tag{9}$$

Solve this boundary value problem and compute η (analytically by hand). Plot η as a function of ϕ (with Matlab).

Answer: $u^*(r) = \cosh(\phi r)/\cosh(\phi/2)$, $u(x_1) = g_D \cosh(\sqrt{\frac{c}{a}}x_1)/\cosh(\sqrt{\frac{c}{a}}\frac{L}{2})$, $\eta = \int_{-1/2}^{1/2} u^*(r)\,dr = \tanh(\phi/2)/(\phi/2)$, $u^*(0) = 1/\cosh(\phi/2)$. Note that $u^*(r) \equiv 1$ and hence $\eta = 1$, if $\phi = 0$.

5. Numerical solution

In general we cannot solve (4) analytically. If we assume that the pellet is a long straight cylinder with an arbitrary cross-section, so that u^* depends only on two variables x_1^*, x_2^*, then we can use our programs to compute *approximate solutions*. Some suggestions:

- Solve (6) with $a^*(x_1^*, x_2^*, x_3^*) \equiv 1$, $c^*(x_1^*, x_2^*, x_3^*) \equiv 1$, and $\phi = 1$ for several cross-sections: circle, rectangle, triangle, or whatever. Compute η for each geometry (use quadrature!). Make sure that the diameter is the same ($= 1$) in each case. Which one has the highest efficiency?
- *Dead core:* a region in the middle of the pellet has very small diffusion coefficient.
  Hint: Consider the domain $\Omega = \{(x_1, x_2) : \sqrt{x_1^2 + x_2^2} < \frac{1}{2}\}$, with core $\Omega_{\text{core}} = \{(x_1, x_2) : \sqrt{x_1^2 + x_2^2} < \frac{1}{5}\}$. In `pdetool`:s *draw mode*, first draw a circle with centre at the origin and radius $\frac{1}{2}$, then draw another circle, also with centre at the origin,

and radius $\frac{1}{5}$. In *PDE mode*, select **Show Subdomain Labels**, from the **PDE** menu. Note that Ω_{core} has one number, say 1, and $\Omega - \Omega_{\text{core}}$ has another number, say 2. We call Ω_{core} and $\Omega - \Omega_{\text{core}}$ *sub-domains* of Ω. The union of the sub-domains is Ω itself. Now, define the function `a_2D.m` such that, e.g., $a^* = 0.1$ on Ω_{core}, and $a^* = 1$ on $\Omega - \Omega_{\text{core}}$ (use the argument `delomradesnummer`). It might be a good idea to make one extra refinement of the triangulation in this case.

- *Poisoning:* a region near the boundary of the pellet has very small rate coefficient, $c^* << 1$ or $c^* = 0$.
- *Hole:* there is a hole in the middle of the pellet, where the diffusion coefficient is very large, $a^* >> 1$, and the reaction rate is zero, $c^* = 0$.
- *Robin boundary conditions:* replace the boundary condition in (1) by Robin boundary conditions. Show that in dimensionless variables (with $g_N = 0$, and g_D constant) this becomes

$$-n^* \cdot (a^* \nabla^* u^*) = \nu(u^* - 1), \quad \text{on } \partial\Omega^*.$$

Express the dimensionless number ν (the *Biot number* for mass transfer) in the original variables. Answer: $\nu = \frac{L\gamma}{a_{\text{ref}}}$.