The Pitfalls of Readily Available Solutions: Physically Consistent Global Analysis of Species Transport from a Spherical Particle[1]

A common mistake when attempting to solve an engineering problem is to look up the solution from a textbook or paper, or to apply a mathematical technique, without carefully considering whether the solution or technique is actually valid. Numerous examples of this mistake arise in the literature on the analysis of the stability of dynamical systems, with some of the most common mistakes to avoid described in control textbooks and in past columns of IEEE Control Systems Magazine [1]–[3]. This column gives an example of a more subtle mistake that can be used for setting up a teachable moment [4] for engineering students with a basic understanding of partial differential equations.

This particular example problem consists of assessing the global asymptotic stability of a system in which in a molecular species being released from the external surface of a particle. The entry or release of molecules to/from the surfaces of particles arises in many industrial processes, from commercial air conditioning systems [5], to the removal of toxic chemicals from waste streams [6,7], to the formation of protein crystals in microfluidic devices [8]. In many of these applications, the concentrations of various species within the particle is of interest, for example, when determining the particle size that optimizes process efficiency or for developing an understanding of the spatiotemporal dynamics in fundamental studies (e.g., [9,10]). If the particle is solid, then the mass transfer of a species through the particle is via diffusion and is described by a linear model [7]. If the particle is a liquid, then the mass transfer of a species through the particle is via convection *and* diffusion, and is described by a highly nonlinear model that is only solvable numerically, in which case the pure diffusion model can be used to compute analytical bounds on the maximum difference in species concentrations within the particle. As the species is released from the external surface of the particle, a concentration gradient develops in the particle, with the lowest concentration being at the external surface of the particle and the highest concentration at its center (see Figure 1).

> Encourage students to employ critical thinking when analyzing global stability, to avoid reaching incorrect conclusions.

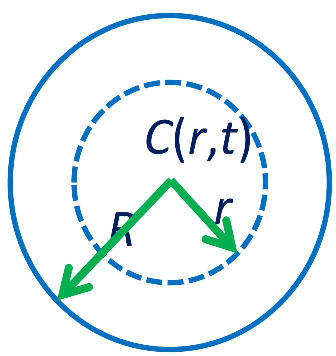

Figure 1. A species of concentration $C(r,t)$ diffusing through a spherical particle of radius R and released from its external surface produces a concentration gradient in the particle. The species

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release at the external particle surface at $r = R$ causes the outer edge of the particle to become less concentrated than its interior.

Neglecting convection, the concentration of a species within an isothermal particle undergoing a constant flux at its external surface is described by the partial differential equation (PDE) known as Fick's second law [11],

$$\frac{\partial C(r,t)}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C(r,t)}{\partial r}\right), \quad 0 \le r \le R, \quad t \ge 0\,, \tag{1}$$

$$C(r, t = 0) = C_0, \quad 0 \le r \le R\,, \tag{2}$$

$$-D\frac{\partial C}{\partial r}(r = R, t) = F, \quad t \ge 0\,, \tag{3}$$

$$\frac{\partial C}{\partial r}(r = 0, t) = 0, \quad t \ge 0\,, \tag{4}$$

where $F > 0$ is the molar flux of a species being released from the external surface of the particle [(moles of species)/(external surface area of particle)(time), mol/m^{2}s], $C(r,t)$ is the species concentration [(moles of species)/(volume of solution), mol/m^3], D is a constant diffusion coefficient of the species through the particle [m^2/s], the radial position r ranges from the center of the particle at $r = 0$ to the outside surface of the particle at $r = R$ [m], and t is time [s]. Fick's second law (1) follows from the insertion of Fick's first law (that is, that flux is proportional to the concentration gradient) into the mass conservation equation for the species molecules in the particle [7]. The initial species concentration C_0 [mol/m^3] is assumed to be spatially uniform in (2) and the particle is assumed to retain its spherical shape. Condition (4) holds due to the assumed spherical symmetry of the particle. The problem statement with model (1)–(4) is described in many publications including in what most engineers would consider the definitive book on the mathematics of diffusion [11].

The species concentration is the state variable in the model (1)–(4). The student problem is to assess whether the system of equations (1)–(4) is *globally asymptotically stable*, that is, whether the state variable $C(r,t)$ approaches a single steady-state value for long time regardless of the value of the initial state $C(r,0) = C_0$.

One way to analyze the global asymptotic stability of a linear PDE that does not require knowledge of Lyapunov theory [12], complex analysis [13], or the generalized Nyquist stability criterion [14] is to analyze the boundedness of the analytical solution for its state variable. An engineer well versed in the solution of mass transfer problems will go to the most widely used book on the mathematics of diffusion [11] to look up the analytical solution for the model (1)–(4), which is given as

$$C(r,t) = C_0 - \frac{FR}{D}\left[\frac{3Dt}{R^2} + \frac{r^2}{2R^2} - \frac{3}{10} - \frac{2R}{r}\sum_{n=1}^{\infty}\frac{\sin(\alpha_n r)}{\alpha_n^2 R^2 \sin(\alpha_n R)}\exp(-D\alpha_n^2 t)\right], \tag{5}$$

where the coefficients α_n are the solutions to

$$\alpha_n R \cot(\alpha_n R) = 1\,. \tag{6}$$

Alternatively, an engineer less familiar with mass transfer problems could directly apply the separation of variables [11] to obtain the analytical solution (5)–(6). For large times, the expression (5) simplifies to

$$C(r,t) = C_0 - \frac{FR}{D}\left[\frac{3Dt}{R^2} + \frac{r^2}{2R^2} - \frac{3}{10}\right]. \tag{7}$$

Based on inspection of either (5) or (7), the obvious answer to the question of global asymptotic stability is that the system is not stable, since each expression has a term that is a linear function of time t with all other terms being bounded for all time. But is this answer correct?

Let's consider the actual physical system in which a species leaves a spherical particle with a nonzero flux over time. A species cannot have a negative concentration, so a physically consistent lower bound on the species concentration $C(r,t)$ is zero. Continuous removal of the species from the particle would eventually deplete the species in the particle, so the species concentration at long time would be expected to approach zero; this physical understanding would suggest that the system is globally asymptotically stable. This asymptotic behavior is in direct contradiction to the analytical solution (5)–(6) reported in the literature that indicates that the species concentration $C(r,t)$ approaches negative infinity as the time t goes to infinity.

Why does analysis based on the analytical solution (5)–(6) produce an incorrect conclusion concerning stability? The key issue is that the original problem statement with model (1)–(4), although published in many papers and textbooks, does not describe a physical problem for all time t. An upper bound for values of the time t when the model (1)–(4) is physically valid can be derived by writing an overall species mass balance on the particle,

$$\frac{4}{3}\pi R^3 C_0 = 4\pi R^2 F t_{\text{u.b.}}, \tag{8}$$

where $4\pi R^3/3$ is the particle volume and $4\pi R^2$ is the external particle surface area. Rearranging this equation implies that the model (1)–(4) cannot be physically valid for any time greater than

$$t_{\text{u.b.}} = \frac{RC_0}{3F}, \tag{9}$$

as any later time would attempt to release more species mass from the particle than was initially in the particle. At this point, a student might try to correct the analytical solution (5)–(6) by including the condition that $t \le \frac{RC_0}{3F}$. Such a condition does not correct the problem, however.

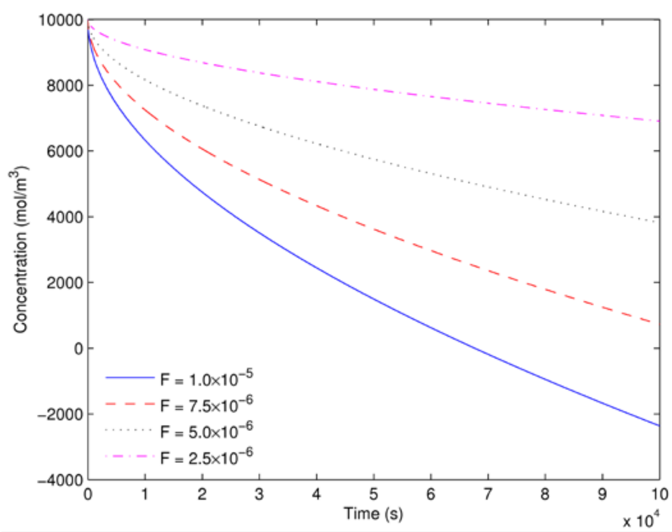

Figure 2. Species concentration at the external surface, $C(R,t)$, in a spherical particle of radius R and with species released from its external surface at four different constant fluxes F, as calculated

from the analytical solution (5)–(6). The values for the other system parameters are given in (10)–(12). The analytical solution is only physically meaningful when the species concentration is nonnegative.

A way to gain an understanding of why such reasoning would be invalid is to inspect Figure 2, which is a plot of the analytical solution (5) for different values for the flux F for

$$C_0 = 10{,}000 \text{ mol/m}^3, \tag{10}$$

$$D = 1.0 \times 10^{-13} \text{ m}^2/\text{s}, \tag{11}$$

$$R = 0.001 \text{ m}. \tag{12}$$

The species concentration becomes negative at some time before $t_{\text{u.b.}} = \dfrac{RC_0}{3F}$. For example, for the flux

$$F = 10^{-5} \text{ mol/m}^2, \tag{13}$$

the species concentration C at the external particle surface $r = R$ computed from (5)–(6) is negative at time $t = 10^5$ seconds, which is less than $\dfrac{RC_0}{3F} = 3.33 \times 10^5$ seconds. This analysis shows that the analytical solution (5)–(6) becomes not physically meaningful at a time much earlier than the time at which all of the species in the particle is depleted. The analytical solution (5)–(6) is only a physically meaningful solution for the model (1)–(4) as long as its predicted species concentration at the surface is nonnegative,

$$C(R,t) \geq 0, \tag{14}$$

which is equivalent to

$$3Dt - 2\sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp(-D\alpha_n^2 t) \leq \frac{DC_0R}{F} - 1.7R^2. \tag{15}$$

Either inequality can be tested at each time t, to assess whether the solution remains physically meaningful. This solution exploits the information that the lowest species concentration occurs at the external surface, which can be argued from physical considerations or by proving that $C(r,t)$ is a monotonically decreasing function in r.

The above discussion focusing on the analytical solution (5)–(6) may give some students the impression that (5)–(6) are somehow at fault, but the problem is really in the original problem statement with model (1)–(4). When the time t is high enough that the inequality (15) is violated, the value of the specified constant flux F becomes higher than is physically possible, that is, higher than the species can diffuse through the particle to reach the external surface. For any constant positive flux at the surface, it is physically impossible for that flux to be constant at long time, due to the limitation in the rate at which the species can diffuse through the particle.

> Encourage students to consider whether a problem statement is physically meaningful before attempting to provide an answer.

Now let's return to the question of global asymptotic stability. We have established that the original problem statement with model (1)–(4) was not physically meaningful when specifying a positive constant flux for all time. So instead consider the problem with the condition that the flux F is always positive but is some function of time that is physically selected so that the species in the particle can diffuse to the external surface at a high enough rate for the flux to be physically achievable. Now let's consider the global asymptotic stability for this modified system.

The simplest way to approach this stability analysis problem is to exploit some physical knowledge about the system, in this case, that the species concentration is directly related to the total mass of species in the particle. An overall species mass balance on the particle is

$$\frac{dm}{dt} = -4R^2 F(t), \tag{16}$$

where

$$m(t) = \int_0^R 4\pi r^2 C(r,t) dr \tag{17}$$

is the total mass of species in the particle and $F(t) > 0, \forall t \geq 0$. The time-derivative of the Lyapunov function $V(m) = m^2$,

$$\frac{dV(m)}{dt} = 2m\frac{dm}{dt} = -8R^2 m(t)F(t) < 0, \forall t, \tag{18}$$

is negative definite, which implies that $m(t) \to 0$ as $t \to \infty$. From (17), this limit implies that

$$\int_0^R r^2 C(r,t) dr \to 0. \tag{19}$$

Since the flux was stated to be physically meaningful, $C(r,t) \geq 0$ for all r. This condition implies that the integrand in (19) is nonnegative for all r, so the limit in (19) can hold only if $C(r,t) \to 0$. This physically consistent system is globally asymptotically stable for any positive flux of species from its surface for all time.

Pedagogical comments

In this particular diffusion problem, global asymptotic stability was proved simply by exploiting physical understanding of the problem. It is important to assign physical problems for analyzing stability to students rather than mathematical abstractions. Otherwise, students will forget to take practical considerations into account once the model has been written, and will turn to a textbook, paper, Mathematica, or the World Wide Web to obtain an analytical solution without evaluating whether the problem statement or its solution is physically meaningful or correct.

– Michael L. Rasche and Richard D. Braatz

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