The Class and Home Problems section is intended to present novel and innovative scenarios that can enhance the teaching of chemical engineering topics. Submissions must have clear learning objectives, outcomes, or similar statements. The fit within a typical chemical engineering (or closely related) curriculum should be clear. Problems may represent a new application of fundamental principles, substantive adaptations that enable effective pedagogical approaches, or new non-proprietary applications of software. Manuscripts should follow the same general guidelines as other *CEE* submissions, but should be submitted directly to Dr. David Silverstein (david.silverstein@uky.edu)

Illustrating the Benefits of Embracing an Integrated Applied Mathematics Initiative: TRANSPORT PARAMETERS, LAPLACE TRANSFORMS, AND RESIDUE THEOREM

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An example problem is presented here to illustrate the relative straightforwardness of a number of viable mathematical concepts often thought of as complex and unwieldy. These are concepts that engineering students often either shy away from—considering them too difficult to apply—or may just simply be unaware of. These knowledge gaps or confidence-level issues can be quite restrictive, and can lead to poor choices with respect to adequately and accurately representing system behavior. Ideally, when en route to obtaining robust solutions to relevant technological problems it is imperative to avoid undue oversimplifications and/or assumptions that can limit a solution's range of applicability, or sometimes even render it essentially useless. Unfortunately, too often systems are modelled using these restrictive approaches. Consequently, the opportunity to obtain the desired robustness is often lost. This can be extremely problematic (a) when evaluating model predictive control (MPC) strategies via simulation protocols and (b) in establishing evaluation criteria for the various design scenarios involved in both process systems and advanced materials development, as these rely upon characterization via transport property determinations (Cussler,[1] Bird, et. al., [2] Deen,[3] and Incropera and DeWitt[4]). This latter issue is particularly relevant in the emerging area of nanotechnology, and specifically in its role in delivery platforms. Representative materials include: (i) smart membranes, as biomimetic systems or as encapsulation materials/surfaces with unique barrier properties; (ii) novel chaperones for drug delivery and controlled release; and (iii) nano-scale entities that are entrapped in macro-scale matrices to produce unique physicochemical properties with enhanced performance characteristics (*e.g.*, Johnson, et. al.,[5] Sokolnicki, et. al.,[6] and Panagiotou and Fisher[7]). Topics such as these are of growing importance, and feature in both core and elective courses offered to support the student's multiple options with respect to concentration tracks.

A number of courses currently available to students as either core or elective provide an excellent opportunity to integrate advanced mathematical tools into a "just in time" scenario along with appropriate applications to maximize students' awareness for potential uses. Collaboration with applied mathematics professionals, such as through curriculum development and co-teaching protocols, is a viable path forward to accomplish our forever evolving program objectives. By embracing the integrated applied mathematics (IAM) program methodologies, the desired modified course offerings with realistic goals and requisite deliverables can be obtained.

The problem selected here for illustration is most appropriate for transport and materials related courses. Its relevance is demonstrated through its role in determining the mass transfer characteristics of specially designed particle systems with specific molecular species selectivity. These particles

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can thus be used in either delivery or sequestration platforms. Furthermore, this problem can serve as a basis for both an in-class example and an extended homework assignment coupled with specific reading material. One scenario that has proven to be successful is to (i) present the "as given" problem in class as an example representative of the delivery platform and (ii) assign as homework the related problem, *i.e.*, representative of the sequestration platform—requiring that students modify the initial and boundary conditions to model an uptake mechanism and to use this analysis protocol as their solution methodology.

It is important to reiterate that use of this problem can assist in meeting a major course objective, *i.e.*, identification of techniques to determine transport properties. The closed-form mathematical solutions obtained here provide the robust equations needed for data analysis, *i.e.*, a critical component of a relatively straightforward methodology to estimate the effective diffusivity of a material. The technique being suggested here is to place the material in a finite volume bath and couple experimental observations with this distributed parameter model representation of the system dynamics. Similar results for a single entity have been previously reported (Cussler,[1] Crank,[8] and Carslaw and Jaeger[9]; see next section for additional comments), but unfortunately the details of their solution methodology are lacking. Therefore, providing such details is a major objective here. That is, this paper intends to further demonstrate the identification and use of an applied mathematical based computational model to evaluate functionalized materials.

The Fickian-based diffusion equation is assumed to be the appropriate partial differential equation to represent the transport mechanism within a given bead. The transient behavior of the coupled finite volume bath, represented by an ordinary differential equation, is the result of the flux from multiple beads and provides a time-dependent boundary condition at each fluid-bead surface interface. It is this coupling through the Eulerian time variable that prompted seeking a solution in the LaPlace domain utilizing deviation variables. Subsequent inversion is accomplished in a straightforward manner through a non-complicated application of the Residue Theorem and the required use of L'Hopital's Rule. Although inversion by the Residue method is not a new concept, it was worthwhile to revisit in conjunction with this example to demonstrate ease of use as well. Furthermore, it should be pointed out that this method can be very useful in efficiently solving systems of nonhomogeneous linear partial differential equations.

RATIONALE/OBJECTIVES

A fairly common misconception is that the LaPlace Transform method is only applicable to ordinary differential equations. This point was specifically driven home while on a consulting assignment. The company wanted to initiate a series of transport characterization studies to evaluate their new, specially designed solids that possess tunable properties. Associated with those studies they needed to develop various commercial-scale process alternatives that, upon selection of optimized operational parameters, would yield products with this wide range of desired material properties. The initial markets sought after were those areas that need products that meet enhanced mass transport performance specification. The primary characteristic necessary, but not sufficient, for these product expectations is tunable effective diffusivities. That is, although other mechanisms are in play with these solids (such as diffusion with immobilization and/or reactive sites distributed throughout), knowing effective diffusivities provides an asymptote/limiting property to base further design criteria upon. Furthermore, this limited case analysis is useful as a guide to develop the solution algorithm for those more complicated situations.

The experimental approach and computational results, in the form of closed analytical solutions, for the analysis of a single spherical particle in a small finite bath, have been reported earlier by Cussler,[1] Crank,[8] and Carslaw and Jaeger.[9] The significance of their approach is that one can obtain the diffusivity (D) of the bead material from the time profile of the bath (experimental data). Their model equations and closed-form solutions were those obtained via classical techniques, such as separation of variables and eigenfunction expansions. Graphical methods are discussed using dimensionless variables such as the mass transfer Fourier number.

A more robust method is to use multiple beads since that will provide a larger concentration response in the bath and therefore greater accuracy. Consequently, this multiple-bead approach was selected as the example problem to demonstrate IAM capabilities with a meaningful problem, as will be stated more precisely in identifying the overall objectives for this project. Providing the details of the methodology used to obtain the solution is necessary to clarify the role that additional mechanisms play in dealing with those complications in any desired modifications. As a simple example, note that the presence of multiple beads alters the system's response in a variety of ways. The number of beads (n) appears in the mass balance, transfer area, and bath-to-bead volume ratio; *i.e.*, affecting each bead's time-dependent boundary condition (at $r = R_0$). The effect is felt in the steady state and overall system dynamics through the system time constants—which are related to the system eigenvalues through the volume ratio. Furthermore, the associated eigenfunctions determine the radial distribution within each bead and therefore the flux from the surface of each bead is clearly coupled with bath dynamics. Consequently, a simple adjustment of the transfer area used with the flux determined from the single bead analysis would lead to erroneous results.

PROBLEM STATEMENT/BACKGROUND

The specific problem selected for illustration is from the field of heterogeneous catalysis/reaction engineering. It is modified slightly from what was presented by Cussler[1] in his text as an example problem. As mentioned earlier, to obtain a more robust

methodology for data analysis, multiple beads are considered. Furthermore, clarifying statements about the assumptions are presented here to establish a better understanding about the relevance of this problem and subsequent results obtained.

Quoting Cussler's original statement: "Example 3.5.3: Effective diffusion coefficients in a porous catalyst pellet. Imagine that we have a porous catalyst pellet containing a dilute gaseous solution. We want to measure the effective diffusion of solute by dropping the pellet into a small, well-stirred bath of a solvent gas and measuring how fast the solute appears in the bath. How can we plot these measurements to find the effective diffusion coefficient?" His solution begins with mass balances for both the pellet and bath, combined with Fick's law and the appropriate boundary conditions. The subsequent mathematical rigor provides the analytical solution needed to prepare the parametric curves used in obtaining a graphical solution. Alternatively, a one-variable optimization process can be executed to find the best value for the effective diffusion coefficient that minimizes the error between the experimental data and the model predictions. In both cases the quality of the data obtained from a well-defined experimental protocol and the appropriateness of the model assumptions are critical in determination of realistic values for the transport properties sought. With respect to the major model assumptions, one needs to realize that in any practical-use environment for catalyst applications three major mechanisms are in play—related to thermodynamics (adsorption/desorption) and rate processes (reaction at the catalyst sites and transport of reactants and products). Consequently, to isolate the transport parameters, both reaction and adsorption processes must be absent from the model formulation as given in the following section. Furthermore, the experimental protocol must be designed to be in a process variable space that reflects the need for the mass transport mechanism to dominate system behavior. That is, the solute molecule must be free to diffuse without immobilization or any chemical reaction taking place. This solute molecule must also be a realistic mimic for both reactant and product species that would be present in the actual catalytic process being studied. All these factors have been taken into consideration in the system representation and solution to the model equations. Also note that additional comments are given as appropriate to clarify critical steps in the algorithm selected for implementation in the following section.

APPROACH/SOLUTION

It is important to reiterate that most chemical engineers—students and professionals—are very familiar with the use of LaPlace Transforms for solving linear ordinary differential equations (ODEs). First exposure to the method is in the undergraduate mathematics course sequence and later in a process control course. Typically the ODE is transformed to an equivalent algebraic equation and a solution obtained in the LaPlace space followed by inversion back to the original space thereby obtaining the desired solution. Most often a table of transforms is involved in this process. Numerous techniques have been developed to extend the table when the particular inversion is not listed. However, they can become quite cumbersome and, unfortunately, inversion becomes problematic for some engineers leading to a shying away from using the LaPlace method. Fortunately, as stressed by Loney[10,11] in a number of published works, "There is an alternate technique, however, that is especially useful when a difficult inversion is to be performed. This method employs a concept that is fundamental in the theory of functions of a complex variable, namely the Residue Theorem." As noted earlier, inversion by the Residue method is not a new concept; however it can be extremely useful in efficiently solving systems of non-homogenous partial differential equations.

The approach taken here is essentially that described by Loney,[10] but with a few minor modifications with appropriate clarification points. Following Mickley, Sherwood, and Reed,[12] Churchill and Brown,[13] and Dettman,[14] the variable s in

$$L\{f(t)\} = F(s) = \int_0^\infty e^{-st} f(t)\,dt \qquad (1)$$

can be interpreted as a complex number; typically $s = i\omega$. Eq. (1) defines F(s) as the LaPlace transform of f(t). Fortunately, F(s) is usually analytic (*i.e.*, has a Taylor series expansion), except for singularities. This is an important point since frequently encountered classes of problems in chemical engineering are described by Sturm-Liouville equations and therefore it is beneficial to know that the transform of a solution to these equations is analytic for all finite s values except at the singularities (*i.e.*, poles) of the system (see examples in Loney[11] and Greenberg[15]).

Beginning with the formal, integral definition of the inverse transform

$$L^{-1}\{F(s)\} = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} F(s)e^{st}ds = f(t) \qquad (2)$$

and taking advantage of results from Complex Integral Calculus that yields the Residue Theorem for the line integral in the complex plane, such as for Eq. (2), one obtains

$$\oint_c f(z)\,dz = 2\pi i\sum\nolimits_j \rho_j \qquad (3)$$

where ρ_j is the residue of F(s) at the pole s_j. A clear explanation of how one arrives at this conclusion can be obtained via details in Greenberg.[15] Also note that these details show that ρ_j can be identified with coefficients in the Laurent expansion. We therefore have from Eqs. (2) and (3)

$$f(t) = L^{-1}\{F(s)\} = \sum\nolimits_{h=0}^{\infty} \rho_n(t) \qquad (4)$$

Even though this concept is firmly grounded in the theory of functions of a complex variable, direct use of complex variables is not always required. A procedure detailed by Loney,[10] as replicated below, avoids the direct use of complex variables.

First rewrite F(s) as a quotient

$$F(s) = P(s)/Q(s) \tag{5}$$

which enables us to quickly identify the singular points (poles) of F(s) and to determine if the degree of Q(s) is at least one greater than that of P(s). This procedure may require power series expansions of both P(s) and Q(s). If the degree of the denominator is at least one greater than that of the numerator, and the poles are simple (singularities of order one), then

$$\rho_n(t) = \frac{P(s_n)}{Q'(s_n)} e^{s_n t} \tag{6}$$

where $Q'(s_n)$ is the derivative of Q(s) at the simple pole s_n. If the poles are of order m (multiple pole),

$$\rho_n(t) = e^{s_n t}\left[A_1 + tA_2 + \frac{t^2 A_3}{2!} + \ldots + \frac{t^{m-1} A_m}{(m-1)!}\right] = e^{s_n t}\sum_{j=1}^{m} A_j \frac{t^{j-1}}{(j-1)!} \tag{7}$$

with the A_j's defined by

$$A_j = \frac{1}{(m-j)}\frac{d^{m-j}}{ds^{m-j}}\left[(s-s_n)^m F(s)\right]_{s=s_n} \quad j = 1,2,\ldots,m \tag{8}$$

Now given these tools, let's proceed to solve the illustrative problem, *i.e.*, the analysis for multiple beads (V_B = volume of a single bead) in a well-stirred (finite volume = V_M) media. By coupling the dynamic response of the bath to that for the beads, a method is established to determine the effective diffusivity of a solute within the bead. Note that for multiple beads (n = # of equal-sized beads with radius r = R_0 and porosity ε) the solution is not just simply adjusting the flux from the single bead analysis via the new transfer area. The eigenvalues are also a function of the number of beads (n) present and, thus, the time response is altered significantly.

The analysis now proceeds as follows (since a lengthy derivation is presented only equations at key steps in the analysis are numbered to avoid awkwardness):

$$0 \le r \le R_o : \frac{\partial C}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) = \frac{D}{r^2}\left[2r\frac{\partial C}{\partial r} + r^2 \frac{\partial^2 C}{\partial r^2}\right] = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \tag{9}$$

Using C for C(r,t), as the concentration in a bead.

@t = 0 $C(r,0) = C_0$; r = 0 C(0,t) is finite or $\frac{\partial C}{\partial r} = 0$

@ r = R_0 $C(R_0,t) = B(t)$; *i.e.*, bath concentration = B(t)

For the bath: given B(0) = 0 @ t = 0

$$V_M \frac{\partial B(t)}{\partial t} = (n)4\pi R_0^2\left(-D\frac{\partial C}{\partial r}\bigg|_{r=R_0}\right) \tag{9a}$$

Where D is the effective diffusivity in the bead, r is the radial dimension, R_0 is the bead radius (interface with the solution), t is time, B(t) is the uniform concentration in the solution phase (volume is V_M), n is the number of beads, each with volume V_B, and $\in$ is bead porosity. When the system reaches its steady state the concentrations in each phase are C_{SS} and B_{SS}.

$$\left\{\begin{array}{l} @ss\ \frac{dB}{dt} = 0 \therefore \frac{\partial C}{\partial r} = 0 \text{ or } C_{SS} \ne f(t) @ R_0 C_{SS} = B_{SS} \\ \text{thus:} \quad nC_0 V_B \in = (V_M + V_B)B_{SS} \quad B_{SS} = C_{SS} = \frac{C_0 V_B \in}{V_M + V_B \in} = \frac{C_0 \frac{4}{3}\pi R_0^3 \in n}{V_M + \frac{4}{3}\pi R_0^3 \in n} \\ C_{SS} = \frac{C_0}{\frac{3V_M}{4\pi R_0^3 \in n} + 1} \quad A' \equiv \frac{3V_M}{4\pi R_0^3 \in n} \Rightarrow \boxed{C_{SS} = \frac{C_0}{A'+1}} \end{array}\right\} \tag{10}$$

To simplify the LaPlace Transform Mapping (L. { .. }) use a deviation variable (U) to obtain a zero initial condition:

$$U \equiv C - C_0, \frac{\partial U}{\partial r} = \frac{\partial C}{\partial r} - \frac{\partial}{\partial r} C_0 \text{ Where} \frac{\partial C_0}{\partial r} \equiv 0 \tag{11a}$$

therefore,

$$\frac{\partial U}{\partial t} = \frac{\partial C}{\partial t} \text{and} \frac{\partial^2 U}{\partial r^2} = \frac{\partial^2 C}{\partial r^2} \text{ so that} \frac{\partial U}{\partial t} = D\left[\frac{\partial^2 U}{\partial r^2} + \frac{2}{r}\frac{\partial U}{\partial r}\right] \tag{11b}$$

with IC & BC's: as follows

$$@t = 0, U = 0; \tag{11c}$$

$$@r = 0, \frac{\partial U}{\partial r} = 0; \tag{11d}$$

$$@r = R_0, U = B - C_0 \tag{11e}$$

Note: if no mass transfer limitation exists in the "external" fluid, then the area need not be corrected for $\in$.

$$V_M \frac{dB}{dt} = 4\pi R_0^2 \left(-D\frac{\partial U}{\partial r}\Big|_{r=R_0}\right)(n) \tag{12}$$

By transforming using T = rU, it now looks as though it's a slab problem, *i.e.*, simpler geometry.

$$\frac{\partial T}{\partial t} = r\frac{\partial U}{\partial t} \text{ and} \frac{\partial T}{\partial r} = r\frac{\partial U}{\partial r} + U \tag{13a}$$

$$\frac{\partial}{\partial r}\left(\frac{\partial T}{\partial r}\right) = \frac{\partial}{\partial r}\left(r\frac{\partial U}{\partial r} + U\right) = r\frac{\partial^2 U}{\partial r^2} + \frac{\partial U}{\partial r} + \frac{\partial U}{\partial r} = r\frac{\partial^2 U}{\partial r^2} + 2\frac{\partial U}{\partial r} = \frac{\partial^2 T}{\partial r^2} \tag{13b}$$

or

$$\frac{1}{r}\frac{\partial^2 T}{\partial r^2} = \frac{\partial^2 U}{\partial r^2} + \frac{2}{r}\frac{\partial U}{\partial r} \therefore \frac{1}{r}\frac{\partial T}{\partial t} = \frac{D}{r}\frac{\partial^2 T}{\partial r^2} \Rightarrow \boxed{\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial r^2}} \tag{13c}$$

With IC & BC's as follows:

$$@t = 0, \ T = 0; \tag{13d}$$

$$@r = 0; \ T = 0; \text{ and} \tag{13e}$$

$$@r = R_0, T = R_0 U = R_0\left(B(t) - C_0\right) \tag{13f}$$

And for the bath:

$$\frac{V_M \dfrac{dB}{dt}}{(n)} = 4\pi R_0^2\left[-D\left(\frac{1}{r}\frac{\partial T}{\partial r} - \frac{U}{r}\right)\right]\Bigg|_{r=R_0} = 4\pi R_0^2\left[-D\left(\frac{1}{r}\frac{\partial T}{\partial r} - \frac{T}{r^2}\right)\right]\Bigg|_{r=R_0} \tag{14}$$

with B = 0 @ t = 0

Now apply LaPlace transform; $L\{T(t,r)\} = \hat{T}(s,r) \Rightarrow s\hat{T} = D\frac{d^2\hat{T}}{dr^2}; @r = 0, \hat{T} = 0, \text{and} r = R_0$

$$\hat{T} = R_0\hat{B}(s) - \frac{R_0}{S}C_0 \tag{15}$$

$$\boxed{\frac{d^2\hat{T}}{dr^2} - \alpha^2\hat{T} = 0} \text{ with } \alpha^2 \equiv \frac{S}{D} \tag{16}$$

$$\text{Seek a solution} \Rightarrow \hat{T} = E\sinh\alpha r + F\cosh\alpha r; \tag{17}$$

$$R_0\hat{B}(s) - \frac{R_0}{S}C_0 = E\sinh\alpha R_0 \tag{18}$$

Note that we need $\hat{B}$ before inversion can take place.

$$L\left\{\frac{dB}{dT}\right\} = S\hat{B} = \frac{4\pi R_0^2}{V_M}\left[\frac{-D}{r}\frac{\partial \hat{T}}{\partial r} + \frac{D\hat{T}}{r^2}\right]\Bigg|_{r=R_0}(n) \tag{19}$$

thus we need:

$$\frac{\partial \hat{T}}{\partial r} = \frac{d}{dr}[E \sinh \alpha r] = \alpha E \cosh \alpha r; \text{ and} \frac{\hat{T}}{r^2} = \frac{E \sinh \alpha r}{r^2} \tag{20}$$

substituting:

$$\hat{B} = (n) = \frac{4\pi R_0^2}{SV_M}\left[\frac{-D}{R_0}\alpha E \cosh \alpha R_0 + \frac{ED \sinh \alpha R_0}{R_0^2}\right](\text{i.e.,@}r = R_0) \tag{21}$$

So now

$$E \sinh \alpha R_0 = (n)\frac{R_0 4\pi R_0^2}{SV_M}\left[\frac{-D}{R_0}\alpha E \cosh \alpha R_0 + \frac{ED \sinh \alpha R_0}{R_0^2}\right] - \frac{R_0 C_0}{S}$$

$$(n)\frac{4\pi R_0^3}{SV_M}\left[\frac{SV_M}{4\pi R_0^3 (n)} E \sinh \alpha R_0 + \frac{D}{R_0}\alpha E \cosh \alpha R_0 - \frac{ED \sinh \alpha R_0}{R_0^2}\right] = -\frac{R_0 C_0}{S} \tag{22a}$$

$$E = \frac{\dfrac{-R_0 C_0}{S}\dfrac{SV_M}{4\pi R_0^3 (n)}}{\left[\dfrac{SV_M}{4\pi R_0^3 (n)} \sinh \alpha R_0 - \dfrac{D \sinh \alpha R_0}{R_0^2} + \dfrac{\alpha D}{R_0} \cosh \alpha R_0\right]} \tag{22b}$$

$$\hat{T} = [E \sinh \alpha R] \text{ and } L^{-1}\{\hat{T}\} = T = rU = r(C - C_0) \tag{23}$$

To accomplish the LaPlace inversion we need to use the Residue Theorem, *i.e.*, find the poles, etc., once $\hat{T}$ is expressed as a ratio of the form

$$\hat{T} = \frac{P(s)}{Q(s)} = \frac{\dfrac{-V_M C_0}{4\pi R_0^2 (n)} \sinh \alpha r\left(\dfrac{4\pi R_0^3}{V_M}(n)\right)}{\left[\left(S - \dfrac{4\pi R_0 D}{V_M}(n)\right)\sinh \alpha R_0 + \dfrac{\alpha D 4\pi R_0^2}{V_m}(n) \cosh \alpha R_0\right]} \tag{24}$$

Thus, we need the poles to invert it! *i.e.*, roots of Q(s) = 0

$$\hat{T} = \frac{-R_0 C_0 \sinh \alpha r}{\left[\left(S - \dfrac{4\pi(n) R_0 D}{V_M}\right)\sinh \alpha R_0 + \dfrac{\alpha D 4\pi R_0^2}{V_M}(n) \cosh \alpha R_0\right]}$$

$$S - \frac{4\pi D R_0}{V_M}(n) = -\frac{\alpha D 4\pi R_0^2}{V_M}(n)\frac{\cosh \alpha R_0}{\sinh \alpha R_0} \tag{25}$$

Using

$$A' = \frac{V_M}{\frac{4}{3}\pi R_0^3 (n) \in} = \text{ratio of volumes}$$

$$S - \frac{3D}{R_0^2 A'} \equiv \frac{-\alpha 3D}{A' R_0}\frac{\cosh \alpha R_0}{\sinh \alpha R_0} \Rightarrow R_0^2 A' S - 3D = \frac{-3\alpha D R_0}{\tanh \alpha R_0} \tag{26a}$$

$$\tanh \alpha R_0 = \frac{-3\alpha D R_0}{-3D + S R_0^2 A'}; \quad \text{recall } S = \alpha^2 D$$

$$\tanh \alpha R_0 = \frac{-3\alpha D R_0}{-3D + R_0^2 A' \alpha^2 D} \tag{26b}$$

$$\text{to simplify use } \alpha = i\lambda, D\lambda^2 = -S; \text{ with } i \equiv \sqrt{-1}$$

$$\text{such that } \tanh i\lambda R_0 = \frac{i \sin \lambda R_0}{\cos \lambda R_0} = i \tan \lambda R_0 = \frac{-3\lambda i R_0}{-3 + R_0^2 A'(-1)\lambda^2} \text{ or}$$

$$\tan \lambda R_0 = \frac{3\lambda R_0}{3 + A' R_0^2 \lambda^2} \tag{26c}$$

Note: $\lambda_m R_0$ are the infinity of roots; with $\lambda = 0$ (S = 0) the steady state solution is obtained: $C_{ss}r$.

Now, concentrate on the $\frac{P(s)}{Q(s)}$ term of $\hat{T}(s)$

$$T = L^{-1}\left\{\hat{T}(s)\right\} = L^{-1}\left\{\frac{P(s)}{Q(s)}\right\} \text{ which will yield } \frac{P(s_n)}{Q'(s_n)} \exp(s_n t) \tag{27}$$

Recall : $s_m = \alpha_m^2 D = -\lambda_m^2 D, (\text{since } \alpha_m = i\lambda_m)$

also use $Q' \equiv \frac{d}{dS} Q$ and

$\Gamma = \beta D = (n)\frac{4\pi R_0}{V_M} D = \frac{3D}{R_0^2 A'}$ with

$A' = \frac{V_M}{(n)\frac{4}{3}\pi \in R_0^3}$ and $\beta = \frac{3}{R_0^2 A'}$

Note that $\sinh(i\lambda_m r) = i \sin(\lambda_m r)$

$$P(s) = -R_0 C_0 \sinh(i\lambda_m r) = -i R_0 C_0 \sin \lambda_m r \tag{28a}$$

$$Q(s) = (s - \Gamma)\sinh(i\lambda_m r) + i\lambda_m R_0 \Gamma \cosh(i\lambda_m R_0) = i\left[(s - \Gamma)\sin \lambda_m R_0 + \lambda_m R_0 \Gamma \cos \lambda_m R_0\right] \tag{28b}$$

$$\frac{P(s)}{Q(s)} = \frac{-R_0 C_0 \sin \lambda_m r}{(s - \Gamma)\sin \lambda_m R_0 + \lambda_m R_0 \Gamma \cos \lambda_m R_0} \tag{28c}$$

for $s_m = 0$ root (i.e., s.s.term) use $\lim_{s \to 0} \frac{sP(s)}{Q(s)}$

$$\lim_{s \to 0} \frac{sP(s)}{Q(s)} = \frac{\lambda_m^2 R_0 C_0 \sin \lambda_m r}{(\lambda_m^2 - \beta)\sin \lambda_m R_0 + \lambda_m R_0 \beta \cos \lambda_m R_0} \tag{29}$$

$s \to 0$ & $\lambda \to 0$ imply the same thing; also $\frac{d}{ds} = \frac{d}{d\lambda}\frac{d\lambda}{ds}$ (30)

so if we use L'Hopital's rule to remove "indeterminate forms," then we can use $\frac{d}{d\lambda}$ & $\lambda \to 0$ [$\frac{d\lambda}{ds}$ terms in numerator (N) and denominator (D) will cancel out (always)].

Applying L'Hopital's rule 3 times;

$$\lim_{\lambda \to 0} \frac{\frac{d^3}{d\lambda^3} N}{\frac{d^3}{d\lambda^3} D} = \lim_{\lambda \to 0} \frac{\left(6R_0 C_0 r - \lambda_m^2 R_0 r^3 C_0\right)\cos \lambda_m r - 6\lambda_m R_0 C_0 r^2 \sin \lambda_m r}{\left(\lambda_m^2 R_0^3 - 2R_0^3 \beta - 6R_0\right)\cos \lambda_m R_0 + \left(6\lambda_m R_0^2 + \lambda_m R_0^4 \beta\right)\sin \lambda_m R_0} \tag{31}$$

$$= \frac{6R_0C_0r}{-2R_0^3\beta - 6R_0} = \frac{-rC_0}{1+\frac{1}{3}\beta R_0^2} \quad \text{recall: } \beta = 3/R_0^2A'$$

$$\frac{-C_0r}{1+\frac{1}{A'}} = \boxed{-\frac{A'C_0r}{A'+1}} \text{ i.e., the } S=0 \text{ term.} \tag{32}$$

Now for the $S_n \neq 0$ terms we need

$$\frac{P(s)}{Q'(s)} \tag{33}$$

$$Q'(s) = \frac{d}{d\lambda}\frac{d\lambda}{ds}\left[-\lambda_m^2 D\sin\lambda_m R_0 - \beta D\sin\lambda_m R_0 + \lambda_m R_0 \beta D\cos\lambda_m R_0\right]$$

$$= \frac{1}{2A'}\left[(2A'+3)\sin\lambda_m R_0 + A'\lambda_m R_0\cos\lambda_m R_0\right] \tag{34a}$$

So:

$$\frac{P(s)}{Q'(s)} = \frac{-2A'R_0C_0\sin\lambda_m r}{\left\{(2A'+3)\sin\lambda_m R_0 + A'\lambda_m R_0\cos\lambda_m R_0\right\}}$$

$$= \frac{-2A'R_0C_0\sin\lambda_m r\sin\lambda_m R_0}{\left\{(2A'+3)\sin^2\lambda_m R_0 + A'\lambda_m R_0\sin\lambda_m R_0\cos\lambda_m R_0\right\}} \tag{34b}$$

Noting:

$$\sin^2 x = \frac{\tan^2 x}{1+\tan^2 x};\ \cos^2 x = \frac{1}{1+\tan^2 x} \&\ \sin x\cos x = \frac{\tan x}{1+\tan^2 x}$$

$$\frac{P(s)}{Q'(s)} = \frac{-2A'R_0C_0\sin\lambda_m r\sin\lambda_m R_0\left(1+\tan^2\lambda_m R_0\right)}{(2A'+3)\tan^2\lambda_m R_0 + A'\lambda_m R_0\tan\lambda_m R_0} \tag{34c}$$

Recall:

$$\tan\lambda_m R_0 = \frac{3\lambda_m R_0}{\left(3+A'R_0^2\lambda_m^2\right)} \equiv \frac{3\lambda_m R_0}{(w)}$$

$$\text{Where: } (w) \equiv 3 + A'R_0^2\lambda_m^2$$

$$\frac{P(s_m)}{Q'(s_m)} = \frac{-\frac{2}{3}A'R_0C_0\left[A'^2R_0^4\lambda_m^4 + (6A'+9)\lambda_m^2R_0^2 + 9\right]\sin\lambda_m r\sin\lambda_m R_0}{(9A'+9)\lambda_m^2R_0^2 + A'^2R_0^4\lambda_m^4} \tag{34d}$$

$$T(t,r) = L^{-1}\left\{\hat{T}(s,r)\right\} = L^{-1}\left\{\frac{P(s)}{Q(s)}\right\} = \sum_{m=0}^{\infty}\frac{P(S_m)}{Q'(S_m)}e^{s_m t} \tag{35}$$

Thus

$$T(t,r) = (-1)\frac{A'C_0r}{A'+1}$$

$$-\frac{2}{3}A'R_0C_0\sum_{m=1}^{\infty}e^{-\lambda_m^2 Dt}\left\{\frac{\left[A'^2R_0^4\lambda_m^4 + 3(2A'+3)\lambda_m^2R_0^2 + 9\right]\sin(\lambda_m r)\sin(\lambda_m R_0)}{\left[A'^2R_0^4\lambda_m^4 + 9(A'+1)\lambda_m^2R_0^2\right]}\right\} \tag{36}$$

and to find C(r,t) recall that

$$U \equiv C(r,t) - C_0 \text{ and } T(r,t) \equiv rU, \text{ i.e., } C(r,t) = U + C_0 = \frac{T}{r} + C_0 \tag{37}$$

1st term, i.e., ss $\Rightarrow \dfrac{-A'C_0}{A'+1} + C_0 = \dfrac{C_0}{A'+1} = C_{ss}$, therefore

$$C(r,t) = \tag{38}$$

$$\boxed{\frac{C_0}{A'+1} - \frac{2}{3r} A' R_0 C_0 \sum_{m=1}^{\infty} \exp\left(-\lambda_m^2 Dt\right) \left\{ \frac{\left[A'^2 R_0^4 \lambda_m^4 + 3(2A'+3)\lambda_m^2 R_0^2 + 9\right] \sin(\lambda_m r) \sin(\lambda_m R_0)}{\left[A'^2 R_0^4 \lambda_m^4 + 9(A'+1)\lambda_m^2 R_0^2\right]} \right\}}$$

To find the bath dynamics we use (from the problem statement):

$$C(R_0, t) = B(t) \tag{39a}$$

$$B(t) = \frac{C_0}{A'+1} - \frac{2A'}{3} C_0 \sum_{m=1}^{\infty} \exp\left(-\lambda_m^2 Dt\right) \{\ \}\Big|_{r=R_0} \tag{39b}$$

for $\{\ \}\Big|_{r=R_0}$ [i.e., see $\{\ \}$ from Eq. 38 for $C(r,t)$] we need

$$\sin^2 \lambda_m R_0 = \frac{\tan^2 \lambda_m R_0}{1 + \tan^2 \lambda_m R_0} = \frac{\dfrac{9\lambda_m^2 R_0^2}{(w)(w)}}{1 + \dfrac{9\lambda_m^2 R_0^2}{(w)(w)}} = \frac{\dfrac{9\lambda_m^2 R_0^2}{(w)(w)}}{\dfrac{\left[(w)(w) + 9\lambda_m^2 R_0^2\right]}{(w)(w)}} = \frac{9\lambda_m^2 R_0^2}{\left[(w)(w) + 9\lambda_m^2 R_0^2\right]}$$

Where: $(w) \equiv 3 + A' R_0^2 \lambda_m^2$, which gives: $\{\ \}\Big|_{r=R_0} = \dfrac{9}{A'^2 R_0^2 \lambda_m^2 + 9(A'+1)}$

Therefore,

$$\boxed{B(t) = \frac{C_0}{A'+1} - 6A'C_0 \sum_{m=1}^{\infty} \frac{\exp\left(-\lambda_m^2 Dt\right)}{\left[A'^2 R_0^2 \lambda_m^2 + 9(A'+1)\right]}} \tag{40}$$

We now have a model equation for the bath dynamics as a function of physical parameters and a transport property. The significance is that one can obtain the effective diffusivity (D) of the bead material from the time profile of the bath, B(t). Through comparison of the experimental data to that predicted by the model we can obtain the best estimate of diffusivity by minimizing the Total Absolute Average Deviation. This is accomplished using a one parameter, non-linear optimization scheme. Of course, graphical methods can be used as discussed in the prior analyses for a single bead. The problem statement and results presented here are consistent with those documented in texts by Cussler,[3] Crank,[8] and Carslaw and Jaeger.[9] Their model equations and closed-form solutions are those obtained via classical techniques, such as separation of variables and eigenfunction expansions. Short- and long-time asymptotes are available; *i.e.*, use of similarity variables (Deen[3] and Incropera and DeWitt[4]) as the initial profile is being developed, and long-time analysis when the first mode dominates (Greenberg[15]), thus using only one exponential term (and other workers[1,3,8,9,11,12]).

An important point to stress is that the use of multiple beads leads to a more robust analysis given the greater magnitude of the bath's response. As discussed earlier, the number of beads (n) appears in the mass balance, transfer area, and volume ratio terms; *i.e.*, affecting each bead's time-dependent boundary condition (at r = R_0). Thus, their presence is reflected/felt in the final equations via the A′ term and λ_m's. The result is altering the steady state and overall system dynamics through both the

bead and bath time constants, which are related to the system eigenvalues through the volume ratio. Also, the associated eigenfunctions determine the radial distribution within each bead and the flux from each bead is clearly coupled with bath dynamics. Thus reiterating: A simple adjustment of the transfer area used with the flux from the single bead analysis would lead to erroneous results.

CONCLUSIONS

Presented here is an example problem that (i) illustrates the ease of use of many mathematical tools for solutions to pertinent technology problems and (ii) is applicable in a number of educational scenarios due to its inherent significance in material characterization studies and the timely insertion of Integrated Applied Mathematical protocols.

Of particular focus was the use of the LaPlace Transform method for solutions to partial differential equations and inversion by the residue method. Although not new concepts, this approach was selected to re-emphasize/demonstrate the usefulness of these methods in efficiently solving systems of moderate complexity without undue oversimplifications.

With respect to the educational aspects, the classroom discussions can focus on coupling IAM with applications related to barrier property characterization, molecular sequestration, and enhanced therapeutic/nutraceutical delivery platforms. The identification and use of IAM-based computational models to evaluate novel functionalized materials developed utilizing, in particular, nanotechnology platform innovations is certainly a growing need in our evolving curriculums. Representative materials include (i) smart membranes, as biomimetic systems or as encapsulating materials/surfaces with unique barrier properties; (ii) novel chaperones for drug delivery and controlled release; and (iii) nano-scale entities that are entrapped in macro-scale matrices to produce unique physicochemical properties with enhanced performance characteristics. Whenever feasible, closed form analytical solutions and/or realistic asymptotes of the governing deterministic model equations should be given in association with the more complex solutions. Guidelines for model reformulations—such as linearization for simplification or enhancing robustness through incorporation of additional complex phenomena, with their associated advanced mathematical representations—are also desirable deliverables that are within realistic objectives.

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