Homework 6

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BIOENG 104 Biological Transport Phenomena | Aaron Streets

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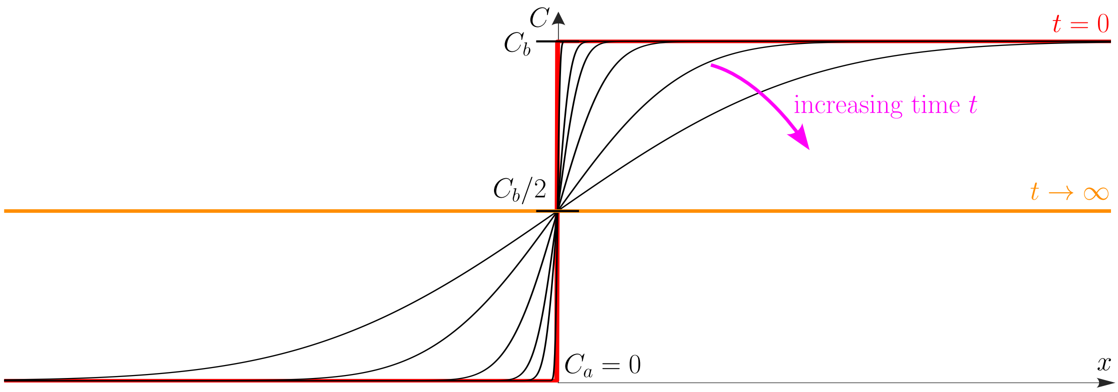
1 Problem 1

A microfluidic channel is infinitely long in both directions and has a valve at $x = 0$ that separates the left half of the channel from the right half. To the left of the valve ($x < 0$) is a solution with no solute ($C_a = 0$) and to the right of the valve is a solution with concentration C_b. At time t=0 the valve is opened and the solute begins to diffuse.

1. In the blank diagram below, draw your estimate for the evolution of $C(x, t)$ at various time points. Mark known values on the X and C axes and include a curve for $t = 0$ and $t \to \infty$.



b) Derive the non-steady state solution for the concentration profile $C(x, t)$ for all x and t. These channels are not well mixed. Confirm that your solution agrees with your drawing, particularly as $t \to \infty$. *Hint:* The portion of the channel to the right (or left) of the valve can be considered as a semi-infinite membrane with partition coefficient $\Phi = 1$.

Assuming that the concentration of solute is dilute everywhere and for all time, we can employ Fick's second law.

$$\frac{\partial C}{\partial t} = D\nabla^2 C + R = D\frac{\partial^2 C}{\partial x^2} + R \tag{1.1}$$

where $R = 0$ is the reaction rate (we also assume there is no reaction occurring). Our boundary conditions are as follows.

$$C(x \to \infty, t > 0) = \Phi C_b = C_b \tag{1.2}$$
$$C(x \to -\infty, t > 0) = \Phi C_a = C_a = 0 \tag{1.3}$$

From Equation (1.1), we can substitute the dimensionless values based on the assumption of semi-infinite medium.

$$\theta = \frac{C(x,t) - C_a}{C_b - C_a}; \qquad \eta = \frac{x}{\sqrt{4Dt}}$$

Using the chain rule, the left hand side of Equation (1.1) can be reexpressed as

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \theta}\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial t} \tag{1.4}$$
$$= (C_b - C_a)\left(-\frac{\eta}{2t}\right)\frac{\partial \theta}{\partial \eta} \tag{1.5}$$

since the partial derivatives of C with respect to θ and η with respect to t are

$$C(x,t) = (C_b - C_a)\theta + C_a \implies \frac{\partial C}{\partial \theta} = C_b - C_a \tag{1.6}$$
$$\frac{\partial \eta}{\partial t} = \frac{x}{\sqrt{4D}}\frac{1}{t^{3/2}}\left(-\frac{1}{2}\right) = \left(-\frac{1}{2t}\right)\frac{x}{\sqrt{4Dt}} = -\frac{\eta}{2t} \tag{1.7}$$

Using the chain rule again, the right hand side of Equation (1.1) can be reexpressed as

$$D\frac{\partial^2 C}{\partial x^2} = D\frac{\partial \eta}{\partial x}\frac{\partial}{\partial \eta}\left(\frac{\partial C}{\partial x}\right) = D\frac{\partial \eta}{\partial x}\frac{\partial}{\partial \eta}\left(\frac{\partial C}{\partial \theta}\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial x}\right)$$
$$= D\frac{1}{\sqrt{4Dt}}\frac{\partial}{\partial \eta}\frac{1}{\sqrt{4Dt}}\frac{\partial^2 \theta}{\partial \eta^2}$$
$$= \frac{C_b - C_a}{4t}\frac{\partial^2 \theta}{\partial \eta^2} \tag{1.8}$$

since the partial derivative of η with respect to x is simply $1/\sqrt{4Dt}$. Gluing Equation (1.5) and Equation (1.8) together gives us

$$(C_b - C_a)\left(-\frac{\eta}{2t}\right)\frac{\partial \theta}{\partial \eta} = \frac{C_b - C_a}{4t}\frac{\partial \theta}{\partial \eta}$$
$$-2\eta\frac{\partial \theta}{\partial \eta} = \frac{\partial^2 \theta}{\partial \eta^2}$$

which is the new differential equation in dimensionless quantities. We can substitute

$u \equiv \partial\theta/\partial\eta$ and integrate twice.

$$
\begin{aligned}
-2\eta &= \frac{1}{u}\frac{\partial u}{\partial \eta} \\
\int -2\eta \,\mathrm{d}\eta &= \int \frac{1}{u}\frac{\partial u}{\partial \eta}\,\mathrm{d}\eta \\
-\eta^2 + \ln A &= \ln u \\
A\mathrm{e}^{-\eta^2} &= u = \frac{\partial \theta}{\partial \eta} \\
\theta &= \int_0^{\eta} A\mathrm{e}^{-z^2}\,\mathrm{d}z + B
\end{aligned}
$$

where $A, B \in \mathbb{R}$ are constants of integration. In terms of these dimensionless quantities, the new boundary conditions are

$$
C(x \to \infty, t > 0) = C_b \implies \theta(\eta \to \infty) = 0 \tag{1.9}
$$

$$
C(x \to -\infty, t > 0) = C_a \implies \theta(\eta \to -\infty) = 1 \tag{1.10}
$$

From both boundary conditions,

$$
\theta(\eta \to \infty) = \int_0^{\infty} A\mathrm{e}^{-z^2}\,\mathrm{d}z + B = 1 \tag{1.11}
$$

$$
\theta(\eta \to -\infty) = \int_0^{-\infty} A\mathrm{e}^{-z^2}\,\mathrm{d}z + B = 0 \tag{1.12}
$$

To solve for A first, we subtract Equation (1.12) from Equation (1.11). We also bring up the Leibniz rule that $\int_{-\infty}^{\infty} \exp\left(-x^2\right)\mathrm{d}x = \sqrt{\pi}$, so

$$
\begin{aligned}
1 &= \int_0^{\infty} A\mathrm{e}^{-z^2}\,\mathrm{d}z - \int_0^{-\infty} A\mathrm{e}^{-z^2}\,\mathrm{d}z \\
&= \int_0^{\infty} A\mathrm{e}^{-z^2}\,\mathrm{d}z + \int_{-\infty}^{0} A\mathrm{e}^{-z^2}\,\mathrm{d}z \\
&= \int_{-\infty}^{\infty} A\mathrm{e}^{-z^2}\,\mathrm{d}z = A\sqrt{\pi} \implies \boxed{A = 1/\sqrt{\pi}}
\end{aligned}
$$

and to solve for B, we plug the value of A back into Equation (1.11).

$$
-\frac{1}{\sqrt{\pi}}\int_0^{\infty} \mathrm{e}^{-z^2}\,\mathrm{d}z + B = 0 \implies \boxed{B = \frac{1}{\sqrt{\pi}}\int_0^{\infty} \mathrm{e}^{-z^2}\,\mathrm{d}z = \frac{1}{\sqrt{\pi}}\frac{\sqrt{\pi}}{2} = \frac{1}{2}}
$$

Therefore, the solution to the system assuming a semi-infinite solution is

$$
\theta(\eta) = \frac{1}{\sqrt{\pi}}\int_0^{\eta} \mathrm{e}^{-z^2}\,\mathrm{d}z + \frac{1}{2} = \frac{1}{2}\operatorname{erf}\eta + \frac{1}{2} = \frac{1}{2}(1 + \operatorname{erf}\eta) \tag{1.13}
$$

and by definition of θ, we can solve for the actual concentration profile,

$$
\begin{aligned}
C(x,t) &= (C_b - C_a)\theta(\eta) + C_a \\
&= \frac{1}{2}(C_b - C_a)(1 + \operatorname{erf}\eta) + C_a
\end{aligned}
$$

$$\boxed{C(x,t) = \frac{C_b}{2}(1 + \operatorname{erf}\eta) = \frac{C_b}{2}\left[1 + \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right]}$$

since $C_a = 0$.

2 Problem 2

Now assume that the microfluidic channel in problem 1 is finite with length $2L$, and with the valve in the middle.

a) Until what critical time, t_c, is it safe to use the solution from the above semi-infinite case, to calculate $C(x,t)$ in this finite case? Assuming this channel has a cross-sectional area of A, calculate the total amount of solute that passes through the open valve between when the valve is opened ($t = 0$) and $t = t_c$. Because we don't have numbers to plug in, use the variables D, L, A, and C_b.

To be safe, let's state that the solution seems to change at around $\eta = 3.0$. Then, by definition of η,

$$\eta = \frac{x}{\sqrt{4Dt_c}} \implies L^2 = 4Dt_c\eta^2 \implies t_c = \frac{L^2}{4D\eta^2} = \boxed{\frac{L^2}{36D}}$$

Recall that flux is the amount of solute passing through a cross-sectional area per unit time. Therefore, using Fick's first law expressed in one dimension, the flux passing through the open valve at $x = 0$ is

$$J_x\Big|_{x=0} = +D\,\frac{\partial C}{\partial x}\Big|_{x=0} \tag{2.14}$$

Therefore, using the chain rule,

$$J_x\Big|_{x=0} = +D\,\frac{\partial C}{\partial \theta}\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial x}\Big|_{\eta=0} = D\frac{C_b - C_a}{\sqrt{4Dt}}\,\frac{\partial \theta}{\partial \eta}\Big|_{\eta=0}$$

Since $\partial\theta/\partial\eta = \mathrm{e}^{-\eta^2}/\sqrt{\pi}$ which was our result in Equation (1.13),

$$J_x\Big|_{x=0} = \sqrt{\frac{D}{4\pi t}}(C_b - C_a) = \sqrt{\frac{D}{4\pi t}}C_b$$

and therefore, the mass of solute that passes through the membrane is

$$\int_0^{t_c} J_x A \, \mathrm{d}t = C_b A \sqrt{\frac{D t_c}{\pi}} = \boxed{\frac{C_b A L}{6\sqrt{\pi}}} \tag{2.15}$$

> b) Now solve for $C(x,t)$ in this finite channel for all t. **Hint:** In this case, the dimensionless parameter θ and the boundary conditions are homogeneous.

We assume that the solute is under a dilute concentration and well-mixed at the initial state. When $t = 0$, the concentrations are initially constant such that the right side at all $x > 0$ has concentration C_b and the left side at all $x < 0$ has concentration $C_a = 0$. For any time t, however, the solute does not flow through the borders of the system. For this reason, the flux at those points ($x = \pm L$) is zero.

$$\begin{aligned} C(x < 0, t = 0) &= C_a = 0 \\ C(x > 0, t = 0) &= C_b \\ J(x = -L, t \geq 0) &= J(x = L, t \geq 0) = 0 \end{aligned}$$

Therefore, since the concentration change is proportional to the flux according to Fick's first law, the concentration gradient at those points must also be zero.

$$\left.\frac{\partial C}{\partial x}\right|_{x=-L} = \left.\frac{\partial C}{\partial x}\right|_{x=+L} = 0$$

To obtain the concentration profile under the finite assumption, we have to find a solution for Fick's second law under the dimensionless quantities.

$$\theta = \frac{C - C_a}{C_b - C_a}; \eta = \frac{x}{L}; \tau = \frac{t}{L^2/D}$$

Similarly to what we started with under the semi-infinite assumption, we start with Fick's second law in one dimension.

$$\frac{\partial C}{\partial t} = D\nabla^2 C = D\frac{\partial^2 C}{\partial x^2} \tag{2.16}$$

The left hand side of the differential equation can be reexpressed as

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \theta}\frac{\partial \theta}{\partial \tau}\frac{\partial \tau}{\partial t} = \frac{D}{L^2}(C_b - C_a)\frac{\partial \theta}{\partial \tau} \tag{2.17}$$

The right hand side of the differential equation can be reexpressed as

$$\begin{aligned} D\frac{\partial^2 C}{\partial x^2} &= D\frac{\partial \eta}{\partial x}\frac{\partial}{\partial \eta}\left(\frac{\partial C}{\partial \theta}\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial x}\right) \\ &= \frac{D}{L}\frac{\partial}{\partial \eta}\left((C_b - C_a)\frac{\partial \theta}{\partial \eta}\frac{1}{L}\right) \\ &= \frac{D}{L^2}(C_b - C_a)\frac{\partial^2 \theta}{\partial \eta^2} \end{aligned} \tag{2.18}$$

So, equating the left hand (2.17) and right hand (2.18) sides together,

$$\frac{D}{L^2}(C_b - C_a)\frac{\partial\theta}{\partial\tau} = \frac{D}{L^2}(C_b - C_a)\frac{\partial^2\theta}{\partial\eta^2}$$
$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\eta^2} \tag{2.19}$$

which is our dimensionless form of the differential equation (1.12). We can start solving for θ right away via the separation of variables method since the boundary conditions (not necessarily the initial conditions) are homogeneous.

$$C(x<0, t=0) = C_a = 0 \implies \theta(\eta<0, \tau=0) = 0$$
$$C(x>0, t=0) = C_b \implies \theta(\eta>0, \tau=0) = 1$$
$$\left.\frac{\partial C}{\partial x}\right|_{x=\pm L} = 0 \implies \left.\frac{\partial\theta}{\partial\eta}\right|_{\eta=\pm 1} = 0 \qquad \textbf{(homogeneous)}$$

The third (boundary) condition follows from

$$\frac{\partial C}{\partial x} = \frac{\partial C}{\partial\theta}\frac{\partial\theta}{\partial\eta}\frac{\partial\eta}{\partial x} = \frac{C_b - C_a}{L}\frac{\partial\theta}{\partial\eta}$$

so $\partial C/\partial x$ is proportional to $\partial\theta/\partial\eta$ for all τ. Under the separation of variables method, we assume that θ is the product of two functions H and T which are dependent on η and τ separately. In other words, $\theta(\eta,\tau) = H(\eta)T(\tau)$. By partial differential equation (2.19),

$$H(\eta)T'(\tau) = H''(\eta)T(\tau) \tag{2.20}$$
$$\frac{H''(\eta)}{H(\eta)} = \frac{T'(\tau)}{T(\tau)} = \text{constant} = \pm\lambda^2 \tag{2.21}$$

Since $H''(\eta)/H(\eta)$ is independent of τ and $T'(\tau)/T(\tau)$ is independent of η, then their equality implies that these ratios have to equal a constant $\pm\lambda^2$ where λ is a real number. This results in two ordinary differential equations:

$$H'' = \pm\lambda^2 H \qquad T' = \pm\lambda^2 T \tag{2.22}$$

We will deal with the case where the constant is $-\lambda^2$. Equation (2.22) on the right is easily solvable by integration,

$$\int \frac{T'}{T}\,\mathrm{d}\tau = \int -\lambda^2\,\mathrm{d}\tau$$
$$\ln T = -\lambda^2\tau + \ln A$$
$$T = A\mathrm{e}^{-\lambda^2\tau}$$

for some constant A.

For H, we use the auxiliary equation of Equation (2.22) on the left, which is $r^2 + \lambda^2 = 0$ (from the equation $H'' + \lambda^2 H = 0$). Thus $r = \pm\lambda i$, so we guess that the solution will be some linear combination of $\mathrm{e}^{i\lambda\eta}$ and $\mathrm{e}^{-i\lambda\eta}$ over $\mathbb{C}$. However, our solution must be a real-valued mapping. Using Euler's formula, we have

$$\mathrm{e}^{i\lambda\eta} = \cos\lambda\eta + i\sin\lambda\eta \qquad \mathrm{e}^{-i\lambda\eta} = \cos\lambda\eta - i\sin\lambda\eta$$

and since both the real and imaginary parts are solutions to the second-order differential equation $H'' + \lambda^2 H = 0$, then any real-valued solution can be constructed as a linear combination of $\cos\lambda\eta$ and $\sin\lambda\eta$. (This also results from the fact that $\cos\lambda\eta$ and $\sin\lambda\eta$ are linearly independent.) Thus, for any pair of real numbers B and C,

$$H = B\cos\lambda\eta + C\sin\lambda\eta$$

and therefore, the combined product of H and T is

$$\begin{aligned} \theta = HT &= A\mathrm{e}^{-\lambda^2\tau}(B\cos\lambda\eta + C\sin\lambda\eta) \\ &= \mathrm{e}^{-\lambda^2\tau}(\alpha\cos\lambda\eta + \beta\sin\lambda\eta) \end{aligned} \tag{2.23}$$

where $\alpha = AB$ and $\beta = BC$. From our boundary conditions, we have that the concentration changes at the edges of the membrane are zero. Since

$$\frac{\partial\theta}{\partial\eta} = \lambda\mathrm{e}^{-\lambda^2\tau}(\beta\cos\lambda\eta - \alpha\sin\lambda\eta)$$

then

$$\left.\frac{\partial\theta}{\partial\eta}\right|_{\eta=1} = \lambda\mathrm{e}^{-\lambda^2\tau}(\beta\cos\lambda - \alpha\sin\lambda) = 0 \tag{2.24}$$

$$\left.\frac{\partial\theta}{\partial\eta}\right|_{\eta=-1} = \lambda\mathrm{e}^{-\lambda^2\tau}(\beta\cos\lambda + \alpha\sin\lambda) = 0 \tag{2.25}$$

which implies that either $\lambda = 0$ or $\beta\cos\lambda \pm \alpha\sin\lambda = 0$. We do not focus on the case where $\lambda = 0$ since this leads to a trivial solution. This implies that (1) $\alpha = 0$ and $\beta\cos\lambda = 0$, or (2) $\beta = 0$ and $\alpha\sin\lambda = 0$. We also note that the case where $\alpha = \beta = 0$ leads to a trivial solution. Therefore, from case (1),

$$\cos\lambda = 0 \implies \lambda = (n + 1/2)\pi,\ n \text{ is a nonnegative integer}$$

and from case (2),

$$\sin\lambda = 0 \implies \lambda = n\pi,\ n \text{ is a nonnegative integer}$$

We can summarize all possibilities that do not lead to trivial solutions as the following:

$$\begin{cases} \alpha \neq 0, \beta = 0, \lambda = n\pi & \text{[set of possibilities 2]} \\ \alpha = 0, \beta \neq 0, \lambda = (n+1/2)\pi & \text{[set of possibilities 1]} \end{cases}$$

We then impose superposition on all possible solutions, labeling the unknown coefficients as α_n and β_n since each coefficient belongs to their own particular solution for each iteration of n. From Equation (2.22),

$$\theta(\eta,\tau) = \sum_{n=0}^{\infty} \alpha_n \mathrm{e}^{-n^2\pi^2\tau}\cos(n\pi\eta) + \beta_n \mathrm{e}^{-\left(n+\frac{1}{2}\right)^2\pi^2\tau}\sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right]$$

Plugging in the boundary conditions where $\theta = 1$ for $\eta > 0$ and $\tau = 0$,

$$\theta(\eta > 0, \tau = 0) = \sum_{n=0}^{\infty} \alpha_n \cos(n\pi\eta) + \beta_n \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] = 1 \tag{2.26}$$

and where $\theta = 0$ for $\eta < 0$ and $\tau = 0$,

$$\theta(\eta < 0, \tau = 0) = \sum_{n=0}^{\infty} \alpha_n \cos(n\pi\eta) + \beta_n \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] = 0 \tag{2.27}$$

This equation is equivalent to

$$\theta(-\eta > 0, \tau = 0) = \sum_{n=0}^{\infty} \alpha_n \cos(n\pi\eta) - \beta_n \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] = 0 \tag{2.28}$$

and therefore, adding Equation (2.26) and Equation (2.28) together, we have

$$\sum_{n=0}^{\infty} 2\alpha_n \cos(n\pi\eta) = 1 \implies \sum_{n=0}^{\infty} \alpha_n \cos(n\pi\eta) = \frac{1}{2}$$

Subtracting Equation (2.28) from Equation (2.26) results in

$$\sum_{n=0}^{\infty} 2\beta_n \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] = 1 \implies \sum_{n=0}^{\infty} \beta_n \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] = \frac{1}{2}$$

To solve for α_n, we can employ the principle of orthogonality. We can treat the integral $\int_0^1 f(x)g(x)\,\mathrm{d}x$, where f and g are functions continuous on $[0,1]$, as an inner product. We can deduce the following properties, where m is a non-negative integer.

$$\int_0^1 \cos(m\pi\eta)\cos(n\pi\eta)\,\mathrm{d}\eta = \begin{cases} 0 & m \neq n \\ 1/2 & m = n \neq 0 \\ 1 & m = n = 0 \end{cases}$$

$$\int_0^1 \sin\left[\left(m+\frac{1}{2}\right)\pi\eta\right]\sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right]\mathrm{d}\eta = \begin{cases} 0 & m \neq n \\ 1/2 & m = n \end{cases}$$

Solving for α_m where $m \neq 0$,

$$\int_0^1 \sum_{n=0}^{\infty} \alpha_n \cos(m\pi\eta)\cos(n\pi\eta)\,\mathrm{d}\eta = \int_0^1 \frac{1}{2}\cos(m\pi\eta)\,\mathrm{d}\eta \implies \frac{1}{2}\alpha_m = \frac{1}{2}\frac{\sin m\pi}{m\pi} = 0 \implies \alpha_m = 0$$

Solving for β_m,

$$\begin{aligned}
\int_0^1 \sum_{n=0}^{\infty} \beta_n \sin\left[\left(m+\frac{1}{2}\right)\pi\eta\right] \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] \mathrm{d}\eta &= \int_0^1 \frac{1}{2} \sin\left[\left(m+\frac{1}{2}\right)\pi\eta\right] \mathrm{d}\eta \\
\frac{1}{2}\beta_m &= -\frac{1}{2} \cdot \frac{\cos[(m+1/2)\pi]-1}{(m+1/2)\pi} \\
\beta_m &= \frac{1}{(m+1/2)\pi}
\end{aligned}$$

since m is an integer and therefore $\cos[(m+1/2)\pi] = 0$. Plugging in the values of $\alpha_n = 0$ and $\beta_n = \left[(m+1/2)\pi\right]^{-1}$, we add a constant α_0 which accounts for the fact that α_m does not necessarily equal to zero when $m = n = 0$, as was deduced earlier in the properties of the inner product.

$$\theta(\eta,\tau) = \sum_{n=0}^{\infty} \frac{1}{(n+\frac{1}{2})\pi} \mathrm{e}^{-\left(n+\frac{1}{2}\right)^2 \pi^2 \tau} \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] + \alpha_0$$

However, we can infer that since, as $\tau \to \infty$, the distribution of θ converges to a uniform distribution at $\theta = 1/2$. So,

$$\theta(\eta,\tau) = \sum_{n=0}^{\infty} \frac{1}{(n+\frac{1}{2})\pi} \mathrm{e}^{-\left(n+\frac{1}{2}\right)^2 \pi^2 \tau} \sin\left[\left(n+\frac{1}{2}\right)\pi\eta\right] + \frac{1}{2} \tag{2.29}$$

By definition of θ,

$$\begin{aligned}
C(x,t) &= (C_b - C_a)\theta(\eta,\tau) + C_a \\
&= C_b\theta(\eta,\tau)
\end{aligned}$$

$$\boxed{C(x,t) = C_b \sum_{n=0}^{\infty} \frac{1}{(n+\frac{1}{2})\pi} \mathrm{e}^{-\left(n+\frac{1}{2}\right)^2 \frac{\pi^2 t}{L^2/D}} \sin\left[\left(n+\frac{1}{2}\right)\frac{\pi x}{L}\right] + \frac{C_b}{2}} \tag{2.30}$$

c) Calculate the following integral.(**Hint:** is this integral a function of time?)

$$\int_{-L}^{L} C(x,t)\,\mathrm{d}x$$

Since we are integrating over a symmetric interval and $C(x,t) - C_b/2$ is an odd function with respect to x according to Equation (2.30),

$$\sin\left[\left(n+\frac{1}{2}\right)\pi\frac{-x}{L}\right] = -\sin\left[\left(n+\frac{1}{2}\right)\pi\frac{x}{L}\right]$$

then all of the integrals with the sinusoidal terms should cancel out to zero.

$$\begin{aligned}\int_{-L}^{L} C(x,t) &= C_b \int_{-L}^{L} \sum_{n=0}^{\infty} \frac{1}{(n+\frac{1}{2})\pi} \mathrm{e}^{-(n+\frac{1}{2})^2 \frac{\pi^2 t}{L^2/D}} \sin\left[\left(n+\frac{1}{2}\right)\frac{\pi x}{L}\right] + \frac{C_b}{2}\,\mathrm{d}x \\ &= C_b \sum_{n=0}^{\infty} \int_{-L}^{L} \frac{1}{(n+\frac{1}{2})\pi} \mathrm{e}^{-(n+\frac{1}{2})^2 \frac{\pi^2 t}{L^2/D}} \sin\left[\left(n+\frac{1}{2}\right)\frac{\pi x}{L}\right] \mathrm{d}x + \int_{-L}^{L} \frac{C_b}{2}\,\mathrm{d}x \\ &= \int_{-L}^{L} \frac{C_b}{2}\,\mathrm{d}x = \frac{C_b}{2}(2L) = \boxed{C_b L}\end{aligned}$$

3 Problem 3

Two well-stirred baths, are connected by a membrane with thickness L and area A. The bath on the left has a volume V_a and starts with a solute concentration C_{a0} at $t = 0$. The bath on the right has a volume V_b and starts with a solute concentration of C_{b0}.

a) Solve for $C_a(t)$, the concentration in the bath on the left as a function of time assuming quasi-steady state diffusion in the membrane.
Assumptions: The diffusivity of solute in the membrane is D and the partition coefficient is ~ 1.0. $V_a \neq V_b$.

We assume that C_{a0} and C_{b0} are dilute concentrations and that the membrane is small enough such that there is a negligible amount of solute within the membrane. Letting $C_a(t)$ be the concentration of bath a at time t and $C_b(t)$ be the concentration of bath b at time t, so that $C_a(t=0) = C_{a0}$ and $C_b(t=0) = C_{b0}$, we can recall Fick's first law from the dilute assumption.

$$J_x(t) = D\frac{C_a(t) - C_b(t)}{L} \tag{3.31}$$

From the small membrane assumption, we have that the mass transfer rate is equal to the rate of change of solute mass inside each membrane.

$$J_x(t)A = -V_a \frac{\mathrm{d}C_a}{\mathrm{d}t} = V_b \frac{\mathrm{d}C_b}{\mathrm{d}t} \tag{3.32}$$

Our goal, essentially, is to express everything in terms of one concentration, namely $C_a(t)$. Due to conservation of mass,

$$V_a C_{a0} + V_b C_{b0} = V_a C_a + V_b C_b \tag{3.33}$$

and therefore, from Equations (3.31) to (3.33),

$$\begin{aligned}-V_a \frac{\mathrm{d}C_a}{\mathrm{d}t} = \frac{DA}{L}(C_a - C_b) &= \frac{DA}{L}\left(C_a - \frac{V_a C_{a0} + V_b C_{b0} - V_a C_a}{V_b}\right) \\ &= \frac{DA}{LV_b}\left[(V_a + V_b)C_a - V_a C_{a0} - V_b C_{b0}\right]\end{aligned}$$

Collecting all the terms with C_a on the same side as $\frac{\mathrm{d}C_a}{\mathrm{d}t}$ and all the other terms on the other side,

$$\frac{1}{(V_a+V_b)C_a - V_aC_{a0} - V_bC_{b0}}\frac{\mathrm{d}C_a}{\mathrm{d}t} = -\frac{DA}{LV_aV_b}$$
$$\frac{1}{V_a+V_b}\ln\left[(V_a+V_b)C_a - V_aC_{a0} - V_bC_{b0}\right] = -\frac{DA}{LV_aV_b}t + \frac{\ln A}{V_a+V_b}$$

where A is a constant of integration.

$$\ln\left[(V_a+V_b)C_a - V_aC_{a0} - V_bC_{b0}\right] = -\frac{DA}{L}\frac{V_a+V_b}{V_aV_b}t + \ln A$$
$$(V_a+V_b)C_a - V_aC_{a0} - V_bC_{b0} = A\exp\left(-\frac{DA}{L}\frac{V_a+V_b}{V_aV_b}t\right)$$

Our initial condition states that $C_a(t=0) = C_{a0}$, so

$$A = (V_a+V_b)C_{a0} - V_aC_{a0} - V_bC_{b0} = V_b(C_{a0} - C_{b0})$$

Therefore,

$$(V_a+V_b)C_a - V_aC_{a0} - V_bC_{b0} = V_b(C_{a0} - C_{b0})\exp\left(-\frac{DA}{L}\frac{V_a+V_b}{V_aV_b}t\right)$$
$$\boxed{C_a(t) = \frac{1}{V_a+V_b}\left[V_aC_{a0} + V_bC_{b0} + V_b(C_{a0} - C_{b0})\exp\left(-\frac{DA}{L}\frac{V_a+V_b}{V_aV_b}t\right)\right]} \tag{3.34}$$

If we let $1/t_b = DA(V_a+V_b)/(LV_aV_b)$, then

$$\boxed{C_a(t) = \frac{1}{V_a+V_b}\left[V_aC_{a0} + V_bC_{b0} + V_b(C_{a0} - C_{b0})\mathrm{e}^{-t/t_b}\right]} \tag{3.35}$$

b) What is the criteria that the thickness of the membrane L must meet in order to use the quasi-steady state assumption, assuming you are given A, D, V_a and V_b? State this criteria in the form of an inequality.

For quasi-steady state to hold, the characteristic time t_b for change in bath concentrations is much much greater than the characteristic diffusion time t_d. From Equation (3.34), we can let the characteristic bath time be

$$\frac{1}{t_b} \equiv \frac{DA}{L}\frac{V_a+V_b}{V_aV_b} \implies t_b = \frac{L}{DA}\frac{V_aV_b}{V_a+V_b} \tag{3.36}$$

and since $t_d = L^2/D$ is the characteristic diffusion time,

$$\begin{aligned} t_b &\gg t_d \\ \frac{L}{DA}\frac{V_aV_b}{V_a+V_b} &\gg \frac{L^2}{D} \\ \frac{1}{A}\frac{V_aV_b}{V_a+V_b} &\gg L \\ \boxed{L \ll \frac{1}{A}\frac{V_aV_b}{V_a+V_b}} \end{aligned} \tag{3.37}$$

What is the total amount of solute that passes through the membrane as $t \to \infty$?

To find the total amount of solute passing through, we compare the concentration of the mass inside the left bath at $t = 0$ and at $t \to \infty$. From Equation (3.34) and the boundary condition,

$$\begin{aligned} C_a(t=0) &= C_{a0} \\ C_a(t\to\infty) &= \lim_{t\to\infty}\frac{1}{V_a+V_b}\left[V_aC_{a0}+V_bC_{b0}+V_b(C_{a0}-C_{b0})\exp\left(-\frac{DA}{L}\frac{V_a+V_b}{V_aV_b}t\right)\right] \\ &= \frac{V_aC_{a0}+V_bC_{b0}}{V_a+V_b} \end{aligned}$$

Therefore, the change in mass is

$$\begin{aligned} \Delta m &\equiv V_a(C_a(t=0)-C_a(t\to\infty)) \\ &= \boxed{V_a\left(C_{a0}-\frac{V_aC_{a0}+V_bC_{b0}}{V_a+V_b}\right)} \end{aligned}$$