Numerical methods in chemistry. Solutions to exercises 6

Problem 1

Using the separation of variables technique, we first find particular solutions. The ansatz

$$\phi(x,t) = X(x)T(t)$$

gives equations for $X(x)$ and $T(t)$ as

$$\frac{T'(t)}{T(t)} = \kappa \frac{X''(x)}{X(x)} = \lambda$$

where λ is the separation constant. This constant must be negative as I will show you at the end. Therefore, we can write $\lambda = -\alpha^2$. The solution of the equation $T'(t) = -\alpha^2 T(t)$ is

$$T(t) = T_0 e^{-\alpha^2 t}, \qquad t \geq 0.$$

A general solution of the equation $X''(x) = \frac{-\alpha^2}{\kappa} X(x)$ for $X(x)$ is

$$X(x) = A\cos\left(\frac{\alpha}{\sqrt{\kappa}}x\right) + B\sin\left(\frac{\alpha}{\sqrt{\kappa}}x\right), \qquad x \in \left[0, \frac{\pi}{4}\right].$$

The second boundary condition, $\phi(0,t) = 0$, implies $X(0) = 0$. Therefore,

$$0 = X(0) = X(x)|_{x=0} = A.$$

The boundary condition $\phi\left(\frac{\pi}{4}, t\right) = 0$ implies $X\left(\frac{\pi}{4}\right) = 0$. Therefore,

$$0 = X\left(\frac{\pi}{4}\right) = X(x)|_{x=\frac{\pi}{4}} = B\sin\left(\frac{\alpha}{\sqrt{\kappa}}\frac{\pi}{4}\right).$$

Because $B \neq 0$ (otherwise the inhomogeneous boundary condition would never be satisfied), we obtain

$$\sin\left(\frac{\alpha}{\sqrt{\kappa}}\frac{\pi}{4}\right) = 0 \Leftrightarrow \frac{\alpha}{\sqrt{\kappa}}\frac{\pi}{4} = n\pi, \qquad n \in \mathbb{N}.$$

We can solve the equation on the right side and obtain

$$\alpha_n = 4n\sqrt{\kappa}.$$

For each $n \in \mathbb{N}$, there is a particular solution

$$\phi_n(x,t) = \tilde{b}_n \sin(4nx)\, e^{-(4n)^2\kappa t}, \qquad \tilde{b}_n = T_0 B_n.$$

Particular solutions will not satisfy the inhomogeneous boundary condition, but an infinite sum of them will (and the sum will still satisfy the homogeneous boundary conditions). Therefore, the general solution is

$$\phi(x,t) = \sum_{n=1}^{\infty} \tilde{b}_n \sin(4nx)\, e^{-(4n)^2\kappa t}.$$

To obtain the coefficients $\tilde{b}_n$, we use the inhomogeneous boundary condition (here the initial condition), leading to

$$\left(\frac{\pi}{4} - x\right) = \phi(x,0) = \phi(x,t)|_{t=0} = \sum_{n=1}^{\infty} \tilde{b}_n \sin(4nx).$$

We express $f(x) = x\left(\frac{\pi}{4} - x\right)$ as a Fourier sine series $f(x) = \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi}{L}x\right)$ in the interval $0 \le x \le L = \frac{\pi}{4}$ in order to satisfy the boundary conditions automatically. Combining the concept of Fourier sine series with the concept of a Fourier series on a general interval, we can compute the b_n's using the expression

$$b_n := \frac{2}{L}\int_0^L x\left(\frac{\pi}{4} - x\right)\sin\left(\frac{n\pi}{L}x\right)dx.$$

The length L of the interval is equal to $\frac{\pi}{4}$ in our specific case. The b_n's then read

$$\begin{aligned}
b_n &= \frac{8}{\pi}\int_0^{\frac{\pi}{4}} x\left(\frac{\pi}{4} - x\right)\sin(4\,n\,x)\,dx \\
&= \frac{8}{\pi}\left\{\left[-\frac{\cos(4\,n\,x)}{4n}\left(\frac{\pi}{4}x - x^2\right)\right]_0^{\frac{\pi}{4}} + \int_0^{\frac{\pi}{4}} \frac{\cos(4\,n\,x)}{4n}\left(\frac{\pi}{4} - 2x\right)dx\right\} \\
&= \frac{8}{\pi}\left\{\left[\frac{\sin(4\,n\,x)}{(4n)^2}\left(\frac{\pi}{4} - 2x\right)\right]_0^{\frac{\pi}{4}} + 2\int_0^{\frac{\pi}{4}} \frac{\sin(4\,n\,x)}{(4n)^2}\right\} \\
&= \frac{8}{\pi}\left[-\frac{2\cos(4\,n\,x)}{(4n)^3}\right]_0^{\frac{\pi}{4}} = \frac{1}{4\pi n^3}\left[1 - \cos(n\pi)\right] = \begin{cases} 0, & n = 2k, \\ \frac{1}{2\pi}\frac{1}{(2k-1)^3}, & n = 2k-1. \end{cases}
\end{aligned}$$

Hence, the Fourier sine series is given by

$$f(x) = \frac{1}{2\pi}\sum_{k=1}^{\infty}\frac{1}{(2k-1)^3}\sin\left[4(2k-1)x\right]$$

and $\phi(x,t)$ satisfies the inhomogeneous boundary condition when $\tilde{b}_n = b_n$. The final solution is therefore given by

$$\phi(x,t) = \frac{1}{2\pi}\sum_{k=1}^{\infty}\frac{1}{(2k-1)^3}e^{-4^2(2k-1)^2\kappa t}\sin\left[4(2k-1)x\right].$$

Proof that the separation constant has to be negative: Assume the separation constant is positive, i.e.,

$$\frac{T'(t)}{T(t)} = \kappa\frac{X''(x)}{X(x)} = \alpha^2.$$

The general solution of the equation $X''(x) = \frac{\alpha^2}{\kappa}X(x)$ for $X(x)$ is

$$X(x) = c_1 e^{\frac{\alpha x}{\sqrt{\kappa}}} + c_2 e^{-\frac{\alpha x}{\sqrt{\kappa}}}.$$

Using the boundary condition $X(0) = 0$, we obtain

$$0 = X(0) = X(x)|_{x=0} = c_1 + c_2.$$

Therefore, $c_2 = -c_1$ and

$$X(x) = c_1 e^{\frac{\alpha x}{\sqrt{\kappa}}} - c_1 e^{-\frac{\alpha x}{\sqrt{\kappa}}} = 2c_1\sinh\left(\frac{\alpha x}{\sqrt{\kappa}}\right).$$

Using the boundary condition $X\left(\frac{\pi}{4}\right) = 0$, we obtain

$$0 = X\left(\frac{\pi}{4}\right) = X(x)|_{x=\frac{\pi}{4}} = 2c_1\sinh\left(\frac{\alpha}{\sqrt{\kappa}}\frac{\pi}{4}\right).$$

Because $\sinh(x) = 0$ only for $x = 0$ (on the real domain), c_1 has to be 0. Therefore,

$$X(x) = 0$$

and the solution would never satisfy the inhomogeneous boundary condition.
In the case of $\alpha^2 = 0$, $X(x)$ is the linear function $X(x) = c_1 x + c_2$. From the boundary conditions $X(0) = 0$ and $X\left(\frac{\pi}{4}\right) = 0$ it follows $X(x) = 0$. This results in the trivial solution $\phi(x,t) = 0$ which does not satisfy the inhomogeneous boundary condition.

Problem 2

Taking the Laplace transform $\Phi(x,s)$ of $\phi(x,t)$ and using the boundary condition $\phi(x,0)=0$ gives the ODE

$$\frac{d^2\Phi(x,s)}{dx^2} = s\Phi(x,s) - \phi(x,0)$$
$$\frac{d^2\Phi(x,s)}{dx^2} = s\Phi(x,s).$$

The general solution of this ODE for $\Phi(x,s)$ reads (you have solved exactly this ODE in Homework 2):

$$\Phi(x,s) = Ae^{-\sqrt{s}x} + Be^{\sqrt{s}x}.$$

From the third boundary condition

$$\lim_{x\to\infty} \phi(x,t) = 0 \tag{1}$$

it follows that $\lim_{x\to\infty} \Phi(x,s) = 0$ and hence [from Eq. (1)] that $B = 0$. Thus, $\Phi(x,s)$ reduces to

$$\Phi(x,s) = Ae^{-\sqrt{s}x}. \tag{2}$$

By taking the Laplace transform of the second boundary condition, $\phi(0,t) = 1$, we get $\Phi(0,s) = \frac{1}{s}$, and therefore [from Eq. (2)] that $A = \frac{1}{s}$.
Finally, $\Phi(x,s)$ can be written as

$$\Phi(x,s) = \frac{1}{s}e^{-\sqrt{s}x},$$

and is inverted thanks to the hint to

$$\phi(x,t) = \text{erfc}\left(\frac{x}{2\sqrt{t}}\right).$$

In[1]:=
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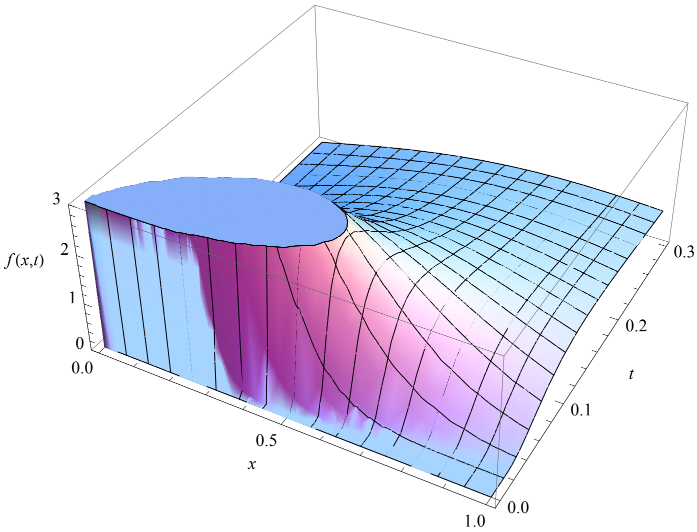
(* Lecture *)
f[x_, t_] = x / (2. Sqrt[Pi t^3]) * Exp[-x^2 / (4 t)] ;
```

In[2]:=
```
Plot3D[f[x, t], {x, -0.001, 1}, {t, -0.001, 0.3},
 PlotRange → {0, 3}, AxesLabel → {x, t, "f(x,t)"}]
```

Out[2]=



In[3]:=
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(* Problem 1 *)
nterms = 10;
f[x_, t_] =
```

$$\frac{1}{2\,\text{Pi}}\,\text{Sum}\left[\frac{1}{(2\,k-1)^3}\,\text{Exp}\left[-16\,(2\,k-1)^2\,t\right]\,\text{Sin}[4\,(2\,k-1)\,x],\ \{k,1,\text{nterms}\}\right]$$

Out[4]=

$$\frac{1}{2\pi}\left(e^{-16t}\,\text{Sin}[4x]+\frac{1}{27}\,e^{-144t}\,\text{Sin}[12x]+\frac{1}{125}\,e^{-400t}\,\text{Sin}[20x]+\frac{1}{343}\,e^{-784t}\,\text{Sin}[28x]+\frac{1}{729}\,e^{-1296t}\,\text{Sin}[36x]+\frac{e^{-1936t}\,\text{Sin}[44x]}{1331}+\frac{e^{-2704t}\,\text{Sin}[52x]}{2197}+\frac{e^{-3600t}\,\text{Sin}[60x]}{3375}+\frac{e^{-4624t}\,\text{Sin}[68x]}{4913}+\frac{e^{-5776t}\,\text{Sin}[76x]}{6859}\right)$$

In[5]:=
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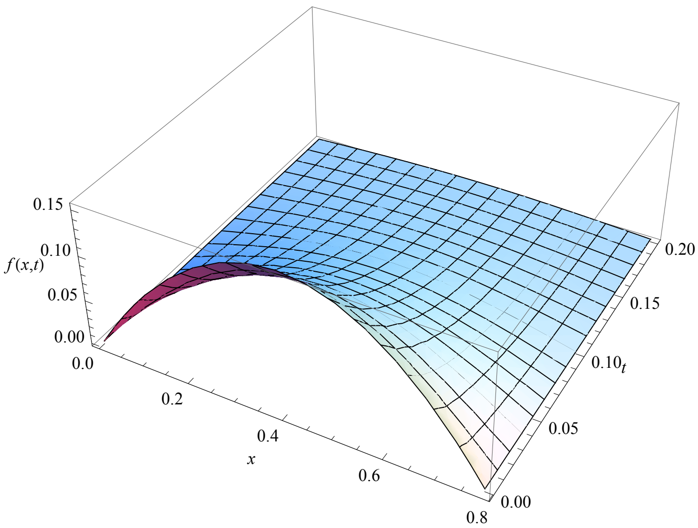
Plot3D[f[x, t], {x, 0, Pi / 4}, {t, 0, 0.2}, AxesLabel → {x, t, "f(x,t)"}]
```

Out[5]=



In[6]:=
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(* Problem 2 *)
f[x_, t_] = Erfc[x / 2. / Sqrt[t]] ;
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In[7]:=
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Plot3D[f[x, t], {x, -0.001, 1}, {t, -0.001, 1},  AxesLabel → {x, t, "f(x,t)"}]
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Out[7]=