# Statistical Mechanics Assignment 7 Solutions

1.

$$
\begin{aligned}
\langle v\rangle &= \sqrt{\frac{8RT}{\pi M}} \\
&= \sqrt{\frac{8(8.314\,5101\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})}{\pi(50\times10^{-3}\,\mathrm{kg/mol})}} \\
&= 355\,\mathrm{m/s}. \\
\therefore \lambda &= 3D/\langle v\rangle \\
&= \frac{3(2\times10^{-9}\,\mathrm{m^2/s})}{355\,\mathrm{m/s}} \\
&= 1.7\times10^{-11}\,\mathrm{m}.
\end{aligned}
$$

This is a tenth the radius of an atom. It's really very small given that distances between molecules in solution tend to be much larger than this (a few atomic radii). One would think that a molecule in solution could move a larger distance than this before hitting another molecule. The gas-phase theory therefore doesn't apply at these densities, not that we expected it to.

2. (a)

$$
\begin{aligned}
\frac{\partial c}{\partial t} &= -D\frac{\alpha\pi^2}{L^2}e^{-\pi^2Dt/L^2}\sin(\pi x/L). \\
\frac{\partial c}{\partial x} &= \frac{\alpha\pi}{L}e^{-\pi^2Dt/L^2}\cos(\pi x/L). \\
\frac{\partial^2 c}{\partial x^2} &= -\frac{\alpha\pi^2}{L^2}e^{-\pi^2Dt/L^2}\sin(\pi x/L).
\end{aligned}
$$

We can see by inspection that

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2},$$

i.e. that $c(x,t)$ satisfies the diffusion equation.

(b) $c(0,t) = c(L,t) = 0$

(c)

$$
\begin{aligned}
J(x,t) &= -D\frac{\partial c}{\partial x} \\
&= -\frac{D\alpha\pi}{L}e^{-\pi^2Dt/L^2}\cos(\pi x/L). \\
\therefore J(0,t) &= -\frac{D\alpha\pi}{L}e^{-\pi^2Dt/L^2}, \\
\text{and}\quad J(L,t) &= \frac{D\alpha\pi}{L}e^{-\pi^2Dt/L^2}.
\end{aligned}
$$

(d) Both fluxes are directed out of the pipe. The rate of loss is therefore

$$-AJ(0,t) + AJ(L,t) = \frac{2AD\alpha\pi}{L} e^{-\pi^2 Dt/L^2}.$$

**Bonus:** To satisfy the boundary conditions, the argument of the sine function must be a multiple of $\pi$ at $x = L$. (The boundary condition at $x = 0$ is automatically satisfied.) That means that the sine function should read $\sin(n\pi x/L)$, where $n$ is an integer (whole number). Then we have

$$\frac{\partial^2}{\partial x^2} \sin(n\pi x/L) = -\frac{n^2\pi^2}{L^2} \sin(n\pi x/L).$$

In order to satisfy the diffusion equation, the exponential in $t$ therefore has to be $e^{-n^2\pi^2 Dt/L^2}$. The general term is then $\alpha_n e^{-n^2\pi^2 Dt/L^2} \sin(n\pi x/L)$. A general solution satisfying these boundary conditions could therefore be constructed by

$$c(x,t) = \sum_n \alpha_n e^{-n^2\pi^2 Dt/L^2} \sin(n\pi x/L).$$

This is basically a Fourier sine series with time-dependent coefficients (if we think of the exponential term as being part of the coefficient of $\sin(n\pi x/L)$).