PHYC90010 - Statistical Mechanics Assignment 3

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Assignment 3 (PHYC90010)
To be handed in by the 17th of May (5pm)

In the stratosphere and mesosphere of the Earth, between altitudes of 30 km and 90 km, solar ultraviolet radiation dissociates oxygen molecules (O_2) to form oxygen atoms (O). An oxygen atom and molecule can then combine to form an ozone molecule in an excited state (O_3^*). In turn, the excited ozone molecule decomposes into its original constituents, unless it collides promptly with some other atmospheric molecule, which carries away the excess energy. The forward and reverse reactions

$$\mathrm{O} + \mathrm{O}_2 \to \mathrm{O}_3^*,$$
$$\mathrm{O}_3^* \to \mathrm{O} + \mathrm{O}_2,$$

proceed with rate coefficients k_1 and k_2 respectively.

(a) Show that the master equation obeyed by the joint probability distribution function $p(x_0, x_3, t)$ of the atomic oxygen (x_0) and ozone (x_3) populations, assuming that the O_2 population is fixed at x_2, is given by [5]

$$\begin{aligned}\frac{\partial p(x_0, x_3, t)}{\partial t} &= k_1 x_2 (x_0 + 1) p(x_0 + 1, x_3 - 1, t) + k_2 (x_3 + 1) p(x_0 - 1, x_3 + 1, t) \\ &- (k_1 x_2 x_0 + k_2 x_3) p(x_0, x_3, t).\end{aligned}$$

(b) Derive the first-order partial differential equation satisfied by the generating function [10]

$$G(t, s_0, s_3) = \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} s_0^{x_0} s_3^{x_3} p(t, x_0, x_3).$$

You should find

$$\frac{\partial G}{\partial t} = k_1 x_2 (s_3 - s_0) \frac{\partial G}{\partial s_0} + k_2 (s_0 - s_3) \frac{\partial G}{\partial s_3}.$$

(c) Assuming that there are exactly p oxygen atoms and zero ozone molecules initially, find the solution for $G(t, s_0, s_3)$. [10]

(d)

i. Calculate the mean number of ozone molecules in equilibrium ($t \to \infty$). [5]

ii. Calculate the covariance $\langle x_0 x_3 \rangle$ at equilibrium ($t \to \infty$). [5]

iii. Are the numbers of oxygen atoms and ozone molecules correlated, anti-correlated, or uncorrelated at equilibrium? Explain the result physically. [5]

Total Marks 40

1 Question 1

1.1 Question 1 - (a)

We know that by definition, $\frac{\partial p(x_0,x_3,t)}{\partial t}$ is given by subtracting the Rate leaving x_0 and x_3 from the Rate entering x_0 and x_3. We know that the rate entering x_0 is given by

$$k_2(x_3+1)p(x_0-1,x_3+1,t),$$

and the rate leaving x_0 is given by

$$k_1x_0x_2p(x_0,x_3,t).$$

Similarly, the rate entering x_3 is given by

$$k_1x_2(x_0+1)p(x_0+1,x_3-1,t),$$

and the rate leaving x_3 is given by

$$k_2x_3p(x_0,x_3,t).$$

By combinging these, we see that this makes the rate of change of the probability function

$$\frac{\partial p(x_0,x_3,t)}{\partial t}=k_1x_2(x_0+1)p(x_0+1,x_3-1,t)+k_2(x_3+1)p(x_0-1,x_3+1,t)-(k_1x_0x_2+k_2x_3)p(x_0,x_3,t) \quad (1)$$

as required.

1.2 Question 1 - (b)

By using a generating function of the form

$$G(t,s_0,s_3)=\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}s_0^{x_0}s_3^{x_3}p(t,x_0,x_3) \quad (2)$$

and substituing it into (1), we can pass the partial differential through the sums, and assuming that the s_0 and s_3 terms are constants in time, we see that

$$\begin{aligned}\frac{\partial G}{\partial t}=&\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}s_0^{x_0}s_3^{x_3}\frac{\partial p}{\partial t}\\ =&k_1x_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}(x_0+1)s_0^{x_0}s_3^{x_3}p(x_0+1,x_3-1,t)+k_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}(x_3+1)s_0^{x_0}s_3^{x_3}p(x_0-1,x_3+1,t)\\ &-k_1x_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}x_0s_0^{x_0}s_3^{x_3}p(x_0,x_3,t)+k_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}x_3s_0^{x_0}s_3^{x_3}p(x_0,x_3,t).\end{aligned}$$

We can now change the terminals on the summation by making the substitutions, $x_0\to x_0-1$ in the first term, and $x_3\to x_3-1$ in the second term, the above becomes

$$\begin{aligned}=&k_1x_2\sum_{x_0=-1}^{\infty}\sum_{x_3=0}^{\infty}x_0s_0^{x_0-1}s_3^{x_3}p(x_0,x_3-1,t)+k_2\sum_{x_0=0}^{\infty}\sum_{x_3=-1}^{\infty}x_3s_0^{x_0}s_3^{x_3-1}p(x_0-1,x_3,t)\\ &-k_1x_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}x_0s_0^{x_0}s_3^{x_3}p(x_0,x_3,t)+k_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}x_3s_0^{x_0}s_3^{x_3}p(x_0,x_3,t).\end{aligned}$$

Now, if we make similar substitutions, where $x_3\to x_3+1$ for the first term, and $x_0\to x_0+1$ for the second term, this becomes

$$\begin{aligned}=&k_1x_2\sum_{x_0=-1}^{\infty}\sum_{x_3=1}^{\infty}x_0s_0^{x_0-1}s_3^{x_3+1}p(x_0,x_3,t)+k_2\sum_{x_0=1}^{\infty}\sum_{x_3=-1}^{\infty}x_3s_0^{x_0+1}s_3^{x_3-1}p(x_0,x_3,t)\\ &-k_1x_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}x_0s_0^{x_0}s_3^{x_3}p(x_0,x_3,t)+k_2\sum_{x_0=0}^{\infty}\sum_{x_3=0}^{\infty}x_3s_0^{x_0}s_3^{x_3}p(x_0,x_3,t).\end{aligned}$$

Now, we note that the probability distribution function cannot have any non-zero value for any x value less than zero. Practically, this means

$$p(x_0, -1, t) = 0 \text{ and}$$
$$p(-1, x_3, t) = 0.$$

Taking this now term by term, we can shift the terminals on the sum back, so that we can collect terms inside one set of sums.

First Term We can shift the x_0 sum in the first term by appealing to the nature of the probability distribution, and we can shift the x_3 sum by separating out the

$$\begin{aligned} k_1 x_2 \sum_{x_0=-1}^{\infty} \sum_{x_3=1}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3+1} p(x_0, x_3, t) &= k_1 x_2 \sum_{x_0=0}^{\infty} \sum_{x_3=1}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3+1} p(x_0, x_3, t) \\ &= k_1 x_2 s_3 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3} p(x_0, x_3, t). \end{aligned}$$

Second Term For the second term, we can perform the same operations on the other variable, giving

$$\begin{aligned} k_2 \sum_{x_0=1}^{\infty} \sum_{x_3=-1}^{\infty} x_3 s_0^{x_0+1} s_3^{x_3-1} p(x_0, x_3, t) &= k_2 \sum_{x_0=1}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0+1} s_3^{x_3-1} p(x_0, x_3, t) \\ &= k_2 s_0 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0} s_3^{x_3-1} p(x_0, x_3, t). \end{aligned}$$

Third Term For the third term, we can simply reshuffle the powers of s_0 to show

$$-k_1 x_2 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_0 s_0^{x_0} s_3^{x_3} p(x_0, x_3, t) = -k_1 x_2 s_0 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3} .p(x_0, x_3, t)$$

Fourth Term Simillarly, for the fourth term, we can simply reshuffle the powers of s_3 to show

$$-k_2 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0} s_3^{x_3} p(x_0, x_3, t) = -k_2 s_3 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0} s_3^{x_3-1} p(x_0, x_3, t).$$

Combining all four terms, this becomes

$$\begin{aligned} =& k_1 x_2 s_3 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3} p(x_0, x_3, t) - k_1 x_2 s_0 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3} p(x_0, x_3, t) \\ &+ k_2 s_0 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0} s_3^{x_3-1} p(x_0, x_3, t) - k_2 s_3 \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0} s_3^{x_3-1} p(x_0, x_3, t) \\ =& k_1 x_2 (s_3 - s_0) \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_0 s_0^{x_0-1} s_3^{x_3} p(x_0, x_3, t) + k_2 (s_0 - s_3) \sum_{x_0=0}^{\infty} \sum_{x_3=0}^{\infty} x_3 s_0^{x_0} s_3^{x_3-1} p(x_0, x_3, t) \\ =& k_1 x_2 (s_3 - s_0) \frac{\partial G}{\partial s_0} + k_2 (s_0 - s_3) \frac{\partial G}{\partial s_3}, \end{aligned}$$

as required.

1.3 Question 1 - (c)

Now, this yields a partial differential equation, which can be solved by the method of characteristics. This is apparently the purview of Applied Mathematical Modelling, which I have not done, so I am attempting this for the first time.

We consider a curve in $r - t$ space which is constant, and therefore make a change of variables from t to r, which gives us a differential equation where

$$\frac{\mathrm{d}G}{\mathrm{d}r} = \frac{\partial G}{\partial t}\frac{\mathrm{d}t}{\mathrm{d}r} + \frac{\partial G}{\partial s_0}\frac{\mathrm{d}s_0}{\mathrm{d}r} + \frac{\partial G}{\partial s_3}\frac{\mathrm{d}s_3}{\mathrm{d}r}$$

Since the curve we are considering is constant, the solution will have the form

$$G(t, s_0, s_3) = [s_0(t = 0)]^p$$

This gives three characteristic equations

$$\frac{\mathrm{d}t}{\mathrm{d}r} = 1 \;\Rightarrow t(r) = r \tag{3}$$

$$\frac{\mathrm{d}s_0}{\mathrm{d}r} = -k_1 x_2 (s_3 - s_0) \tag{4}$$

$$\frac{\mathrm{d}s_3}{\mathrm{d}r} = -k_2(s_0 - s_3) \tag{5}$$

The (4) and (5) are coupled ODE's, which we can solve by treating them as a system of equations. Reexpressing them in terms of $a = -k_1 x_2$ and $b = -k_2$ for convenience they become

$$\frac{\mathrm{d}s_0}{\mathrm{d}r} = a(s_3 - s_0) \tag{6}$$

$$\frac{\mathrm{d}s_3}{\mathrm{d}r} = b(s_0 - s_3) \tag{7}$$

Now, rearranging (6), we see

$$s_0 = s_3 - \frac{1}{a}\frac{\mathrm{d}s_0}{\mathrm{d}r}. \tag{8}$$

Now, if we substitute this into (7), it becomes

$$\begin{aligned}\frac{\mathrm{d}s_3}{\mathrm{d}r} &= b(\cancel{s_3} - \frac{1}{a}\frac{\mathrm{d}s_0}{\mathrm{d}r} - \cancel{s_3})\\ \frac{\mathrm{d}s_3}{\mathrm{d}r} &= -\frac{b}{a}\frac{\mathrm{d}s_0}{\mathrm{d}r}\end{aligned}$$

$$\Rightarrow s_3 = -\frac{b}{a}s_0 + C_1 \tag{9}$$

Substituting (9) into (6) gives

$$\begin{aligned}\frac{\mathrm{d}s_0}{\mathrm{d}r} &= a(-\frac{b}{a}s_0 + C_1 - s_0)\\ &= -bs_0 + aC_1 - as_0\\ \frac{\mathrm{d}s_0}{\mathrm{d}r} &= -(a+b)s_0 + aC_1\\ \frac{\frac{\mathrm{d}s_0}{\mathrm{d}r}}{aC_1 - (a+b)s_0} &= 1\\ \Rightarrow -\frac{\log(aC_1 - (a+b)s_0(r))}{a+b} &= r + C_2\end{aligned}$$

Note that above, we obtain $s_3(r)$ from (9) for free.

$$\Rightarrow s_0(r) = \frac{a}{a+b}C_1 + C_2 e^{-(a+b)t} \tag{10}$$

$$\Rightarrow s_3(r) = \frac{a}{a+b}C_1 - \frac{b}{a}C_2 e^{-(a+b)t} \tag{11}$$

Now, rearranging (10) and (11), and setting $a + b = \beta$ for convenience, we can obtain a value for C_2, and we get the expression for C_1 from (9)

$$\begin{aligned}
s_3 - s_0 &= \frac{b}{a} C_2 e^{-\beta t} + C_2 e^{-\beta t} \\
&= \frac{a+b}{a} C_2 e^{-\beta t} \\
\Rightarrow C_2 &= -\frac{a}{\beta}(s_3 - s_0) e^{-\beta t} \\
\Rightarrow C_1 &= s_3 + \frac{b}{a} s_0
\end{aligned}$$

Now, since we want to find the solution on the constant curve, and we know that the initial number of oxygen atoms is p, then the solution will be some constant value, defined by the value of the generating function for that condition. Therefore

$$\begin{aligned}
G(t, s_0, s_3) &= [s_0(t=0)]^p \\
&= \left[\frac{a}{\beta} C_1 - C_2\right]^p \\
&= \left[\frac{a}{\beta}(s_3 + \frac{b}{a} s_0) - \frac{a}{\beta}(s_3 - s_0) e^{-\beta t}\right]^p \\
&= \left[\frac{(-b s_0 - a s_3)(1 - e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right]^p \\
&= \left[\frac{(k_2 s_0 + k_1 x_2 s_3)(1 - e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right]^p
\end{aligned}$$

1.4 Question 1 - (d)

1.4.1 Question 1 - (d) - i

We can compute the mean number of ozone molecules by using the generating function

$$\begin{aligned}
\langle x_3 \rangle &= \left.\frac{\partial G}{\partial s_3}\right|_{s_0 = s_3 = 1} \\
&= \frac{\partial}{\partial s_3}\left[\left(\frac{(k_2 s_0 + k_1 x_2 s_3)(1 - e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right)^p\right] \\
&= p\left(\frac{(k_2 s_0 + k_1 x_2 s_3)(1 - e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right)^{p-1}\left(\frac{k_1 x_2 (1 - e^{-\beta t})}{\beta}\right) \\
&= p\left(\frac{\cancel{\beta}(1 - e^{-\beta t})}{\cancel{\beta}} + s_0 e^{-\beta t}\right)^{p-1}\left(\frac{k_1 x_2 (1 - e^{-\beta t})}{\beta}\right)
\end{aligned}$$

Now taking the mean in equilibrium, we take the limit where $t \to \infty$, which becomes

$$\begin{aligned}
\langle x_3 \rangle \Big|_{t\to\infty} &= \lim_{t\to\infty}\left[p\left((1 - e^{-\beta t}) + s_0 e^{-\beta t}\right)^{p-1}\left(\frac{k_1 x_2 (1 - e^{-\beta t})}{\beta}\right)\right] \\
&= \left[p\left((1 \cancel{- e^{-\beta t}}) \cancel{+ s_0 e^{-\beta t}}\right)^{p-1}\left(\frac{k_1 x_2 (1 \cancel{- e^{-\beta t}})}{\beta}\right)\right] \\
&= p[1]^{p-1}\frac{k_1 x_2}{k_2 + k_1 x_2} \\
&= \frac{p k_1 x_2}{k_2 + k_1 x_2}
\end{aligned}$$

1.4.2 Question 1 - (d) - ii

Similarly, in order to compute the cross correlation, we use the generating function, in the form

$$\langle x_0 x_3 \rangle = \left.\frac{\partial^2 G}{\partial s_0 \partial s_3}\right|_{s_0 = s_3 = 1} - \langle x_0 \rangle \langle x_3 \rangle$$

In order to compute this, we first need to find $\langle x_0 \rangle$, which we do in the same method as above

$$
\begin{aligned}
\langle x_0 \rangle &= \left.\frac{\partial G}{\partial s_0}\right|_{s_0=s_3=1} \\
&= \frac{\partial}{\partial s_0}\left[\left(\frac{(k_2 s_0 + k_1 x_2 s_3)(1-e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right)^p\right] \\
&= p\left(\frac{(k_2 s_0 + k_1 x_2 s_3)(1-e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right)^{p-1}\left(k_2(1-e^{-\beta t}) + e^{-\beta t}\right) \\
&= p\left(\frac{\cancel{\beta}(1-e^{-\beta t})}{\cancel{\beta}} + s_0 e^{-\beta t}\right)^{p-1}\left(\frac{k_2}{\beta}(1-e^{-\beta t}) + e^{-\beta t}\right)
\end{aligned}
$$

Again, finding the long term behaviour gives us

$$
\begin{aligned}
\langle x_0 \rangle &= \lim_{t\to\infty}\left[p\left((1\cancel{-e^{-\beta t}}) + \cancel{s_0 e^{-\beta t}}\right)^{p-1}\left(\frac{k_2}{\beta}(1\cancel{-e^{-\beta t}}) + \cancel{e^{-\beta t}}\right)\right] \\
&= p\,[1]^{p-1}\,\frac{k_2}{\beta} \\
&= \frac{pk_2}{\beta}
\end{aligned}
$$

Now, we have to find $\frac{\partial^2 G}{\partial s_0 \partial s_3}$. Taking the solution found in 1.4.2, we can see

$$
\begin{aligned}
\frac{\partial^2 G}{\partial s_0 \partial s_3} &= \frac{\partial}{\partial s_0}\left[p\left(\frac{(k_2 s_0 + k_1 x_2 s_3)(1-e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right)^{p-1}\left(\frac{k_1 x_2(1-e^{-\beta t})}{\beta}\right)\right] \\
&= p(p-1)\left(\frac{(k_2 s_0 + k_1 x_2 s_3)(1-e^{-\beta t})}{\beta} + s_0 e^{-\beta t}\right)^{p-2}\left(\frac{k_1 x_2(1-e^{-\beta t})}{\beta}\right)\left(\frac{k_2}{\beta}(1-e^{-\beta t}) + e^{-\beta t}\right)
\end{aligned}
$$

Again, taking the behaviour as $t \to \infty$, this becomes

$$
\begin{aligned}
\frac{\partial^2 G}{\partial s_0 \partial s_3} &\to p(p-1)[1]^{p-2}\frac{k_1 x_2}{\beta}\frac{k_2}{\beta} \\
&= p(p-1)\frac{k_1 k_2 x_2}{\beta^2}
\end{aligned}
$$

Now, substituting into our expression for $\langle x_0 x_3 \rangle$, we see that it becomes

$$
\begin{aligned}
\langle x_0 x_3 \rangle &= p(p-1)\frac{k_1 k_2 x_2}{\beta^2} - \frac{p(k_1 x_2)}{\beta} p \frac{k_2}{\beta} \\
&= p(p-1)\frac{k_1 k_2 x_2}{\beta^2} - \frac{p^2(k_1 k_2 x_2)}{\beta^2} \\
&= -p\frac{k_1 k_2 x_2}{\beta^2}
\end{aligned}
$$

1.4.3 Question 1 - (d) - iii

Since the answer for the covariance found in 1.4.3 is negative, this suggests that the number of ozone molecules and oxygen molecules are anti-correlated at equilibrium. This makes sense, since physically, provided there are only a fixed number of oxygen atoms in the system, the amount of ozone molecules will go up as the number of oxygen molecules go down, and vice-versa.