Statistical physics

lecture 13

Szymon Stoma

25-01-2010

X

Problem:

$$R_1, k_1 : S \rightarrow \emptyset$$

Solution:

$$[S] = S_0 e^{-k_0 t}$$

where S_0 is an inititial concentration of S and k_0 is a kinetic constant.

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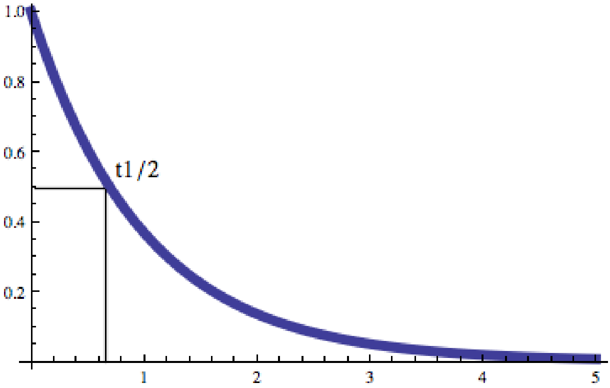

X

$$S(t_{1/2}) = S_0/2$$

$$S_0 e^{-k_0 t_{1/2}} = S_0/2$$

$$e^{-k_0 t_{1/2}} = 1/2$$

$$e^{-k_0 t_{1/2}} = e^{ln 1/2}$$

$$-k_0 t_{1/2} = ln 1/2$$

$$t_{1/2} = ln 2^{-1} / - k_0$$

$$t_{1/2} = ln 2 / k_0$$

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X

n - number of S particles
$P(n)$ - probability of having n particles of S
$P(n,t)$ - probability of having n particles of S in the time t
What are the possible transitions of the system?

X

From Master equation we can write:

$$\frac{\partial P(n,t)}{\partial t} = w_{n,n+1}P(n+1,t) - w_{n-1,n}P(n,t)$$

$w_{n,k}$ - rate of change from state k into n

We can assume: $w_{n,n+1} \sim n+1$ and $w_{n-1,n} \sim n$.

$$\frac{\partial P(n,t)}{\partial t} = (n+1)P(n+1,t) - nP(n,t)$$

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Our target is to compute $P(n,t)$. We know:

$$\frac{\partial P(n,t)}{\partial t} = w_{n,n+1}P(n+1,t) - w_{n-1,n}P(n,t)$$

$P(n_0,0) = 1, \forall i \neq 0. P(n_i,0) = 0$

No particles of S are created during the decay process.

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We define generating funtion:

$$G(s,t) = \sum_{n=0}^{n_0} P(n,t) s^n$$

$$\frac{\partial G(s,t)}{\partial t} = \sum_{n=0}^{n_0} \frac{\partial P(n,t)}{\partial t} s^n$$

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X

It can be shown:

$$\frac{\partial G}{\partial t} = k(1 - s)\frac{\partial G}{\partial s}$$

X

Since $\forall i \neq 0 . P(n_i, 0) = 0$:

$$G(s, t = 0) = \sum_{n=0}^{n_0} P(n, 0) s^n = P(n_0, 0) s^{n_0}$$

Since $P(n_0, 0) = 1$:

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We define:

- $\tau(t) = kt$
- $\sigma(s) = -ln(1-s)$

We can derivate these functions:

- $d\tau = kdt$
- $d\sigma = 1/(1-s)$ (note: $(fg)'(x) = f'(g(x))g'(x)$)

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Fact

It can be shown that:

$$\frac{\partial G}{\partial \sigma} = \frac{\partial G}{\partial \tau}$$

X

It can be shown that if:

$$\frac{\partial G}{\partial \sigma} = \frac{\partial G}{\partial \tau}$$

Then all functions which are solution must obey:

$$G(\sigma, \tau) = G(\sigma + \tau) = G(y)$$

X

$$\frac{\partial G}{\partial \sigma} = \frac{dG}{dy}\frac{\partial y}{\partial \sigma} = \frac{dG}{dy}\frac{\partial(\sigma+\tau)}{\partial \sigma} = \frac{dG}{dy}\left(\frac{\partial \sigma}{\partial \sigma} + \frac{\partial \tau}{\partial \sigma}\right) = \frac{dG}{dy}(1+0) = \frac{dG}{dy}$$

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$$\sigma = -ln(1-s)$$

$$e^{\sigma} = e^{-ln(1-s)}$$

$$e^{\sigma} = (1-s)^{-1}$$

$$1 - s = e^{-\sigma}$$

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From the beginning we know that $G(s, 0) = s^{n_0}$. From previous we know: $s = 1 - e^{-\sigma}$ Then we can write:

$$G(\sigma, \tau = 0) = s^{n_0} = (1 - e^{-\sigma})^{n_0}$$

Which allow us (together with $G(\sigma, \tau) = G(\sigma + \tau)$) to write:

$$G(\sigma, \tau) = (1 - e^{-(\sigma+\tau)})^{n_0}$$

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We go back to the G function:

- $G(\sigma,\tau) = (1 - e^{-(\sigma+\tau)})^{n_0}$
- $G(\sigma,\tau) = (1 - e^{-\sigma}e^{-\tau})^{n_0}$
- $G(\sigma,\tau) = \left(1 - e^{ln(1-s)}e^{-kt}\right)^{n_0}$
- $G(\sigma,\tau) = \left(1 - (1-s)e^{-kt}\right)^{n_0}$

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So we have:

$$G(s,t) = \left(1 - (1-s)e^{-kt}\right)^{n_0}$$

And we can check:

- $G(s,t)|_{s=1} = \left(1 - (1-1)e^{-kt}\right)^{n_0} = 1^{n_0} = 1$

X

The first derivate of G over s is the mean:

- $\frac{\partial G(s,t)}{\partial s}|_{s=1} = n_0 \left(1 - (1-s)e^{-kt}\right)^{n_0-1} \left(e^{-kt}\right)|_{s=1}$
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X

The variance is:

- $\sigma^2 = \left(\frac{\partial^2 G}{\partial s^2} + \frac{\partial G}{\partial s} - \left(\frac{\partial G}{\partial s} \right)^2 \right) |_{s=1}$
- $\frac{\partial^2 G}{\partial^2 s} = \frac{\partial \left[n_0 \left(1-(1-s)e^{-kt} \right)^{n_0 - 1} \left(e^{-kt} \right) \right]}{\partial s}$
- $\frac{\partial^2 G}{\partial^2 s} = n_0(n_0 - 1) \left(1 - (1 - s)e^{-kt} \right)^{n_0 - 2} \left(e^{-kt} \right) \left(e^{-kt} \right)$
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- $\sigma^2 = n_0^2 e^{-2kt} - n_0 e^{-2kt} + n_0 e^{-kt} - n_0^2 e^{-2kt}$

X

The variance is:

- $\sigma^2 = \left(\frac{\partial^2 G}{\partial s^2} + \frac{\partial G}{\partial s} - \left(\frac{\partial G}{\partial s}\right)^2 \right) |_{s=1}$
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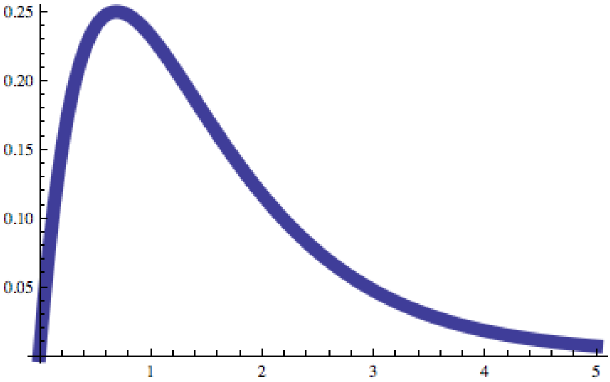
X



X

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- if $t \to 0 : \sigma \to 0$
- if $t \to \infty : \sigma \to 0$
- $\frac{d\sigma^2}{dt} = 0$ to find when the variance is the highest

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- $\sigma^2 = -n_0 e^{-2kt} + n_0 e^{-kt}$
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- $0 = e^{-2kt} * -2 + e^{-kt}$
- $0 = e^{-kt} * -2 + 1$
- $t = ln(2)/k = t_{1/2}$

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- $\sigma^2_{max} = -n_0 e^{-2kt_{1/2}} + n_0 e^{-kt_{1/2}}$
- $\sigma^2_{max} = -n_0 e^{-2ln(2)} + n_0 e^{-ln(2)}$
- $\sigma^2_{max} = n_0/4$
- $\frac{\partial G}{\partial s}|_{s=1,t=t_{1/2}} = n_0 e^{-ln(2)} = n_0/4$
- Max standard error: $\sqrt{(n_0/4)}/(n_0/2) = 1/\sqrt{n_0}$

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- $\sigma / \frac{\partial G}{\partial s}|_{s=1} = \sqrt{n_0 e^{-kt}(1 - e^{-kt})} / (n_0 e^{-kt})$
- $\sigma / \frac{\partial G}{\partial s}|_{s=1} = (1/\sqrt{n_0}) \sqrt{(1 - e^{-kt})} / \sqrt{e^{-kt}}$
- $\sigma / \frac{\partial G}{\partial s}|_{s=1} = (1/\sqrt{n_0}) \sqrt{(e^{kt} - 1)}$
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