

Statistical Physics IV: Non-equilibrium statistical physics
ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)

Solutions to Exercise No.7

7.1 Solution: Master equation for an asymmetric random walk

1. The asymmetric random walk is a birth death process with $g_n = \alpha$ and $r_n = \beta$. Then, the master equation for the continuous-time random walk is given by

$$\frac{\partial}{\partial t} P_n(t) = \alpha P_{n-1}(t) + \beta P_{n+1}(t) - (\alpha + \beta) P_n(t) \quad (1)$$

This master equation can be solved by the method of the generating function ³

$$G(z, t) = \sum_{n \in \mathbb{Z}} z^n P_n(t) \quad (2)$$

Consequently, $P_n(t)$ is given by the z^n coefficient of the Laurent series of $G(z, t)$. The corresponding equation for the generating function $G(z, t)$ is given by

$$\begin{aligned} \frac{\partial}{\partial t} G(z, t) &= \sum_{n \in \mathbb{Z}} z^n \frac{\partial}{\partial t} P_n(t) \\ &\stackrel{\text{Eq.(1)}}{=} \alpha \sum_{n \in \mathbb{Z}} \underbrace{z^n P_{n-1}(t)}_{= z z^{n-1} P_{n-1}(t)} + \beta \sum_{n \in \mathbb{Z}} \underbrace{z^n P_{n+1}(t)}_{= \frac{1}{z} z^{n+1} P_{n+1}(t)} - (\alpha + \beta) \underbrace{\sum_{n \in \mathbb{Z}} z^n P_n(t)}_{= G(z, t)} \\ &= \left(\alpha z + \frac{\beta}{z} - \alpha - \beta \right) G(z, t). \end{aligned}$$

2. To solve this equation, we have to fix an initial condition. If the particle is in n_1 at $t = 0$, the transition probability $P(n_1 | n, t)$ of the process satisfies $P(n_1 | n, t = 0) = \delta_{n_1, n}$, which corresponds to

$$G(z, t = 0) = \sum_{n \in \mathbb{Z}} z^n \delta_{n, n_1} = z^{n_1}$$

In conclusion, the corresponding generating function is

$$G(z, t) = z^{n_1} e^{\left(\alpha z + \frac{\beta}{z} - \alpha - \beta \right) t} \quad (3)$$

3. With $\beta = 0$ we can expand the generating function Eq.(3) in the form of a Laurent series, we find:

$$G(z, t) = \sum_{n=0}^{\infty} z^{n+n_1} \frac{e^{-\alpha t} (\alpha t)^n}{n!} = \sum_{n_2=n_1}^{\infty} z^{n_2} \frac{e^{-\alpha t} (\alpha t)^{n_2-n_1}}{(n_2-n_1)!}$$

where for the last step we have made a change of variable with $n_2 = n + n_1$. Now comparing to the generic of Eq.(2) we conclude:

$$P(n_2, t) = \begin{cases} e^{-\alpha t} \frac{(\alpha t)^{n_2-n_1}}{(n_2-n_1)!}, & n_2 \geq n_1, \\ 0, & n_2 < n_1. \end{cases}$$

7.2 Solution: Equilibrium between photons and atoms

1. From the transition rate we can easily get the master equation:

$$\frac{\partial P_n}{\partial t}(t) = n\gamma N_2 P_{n-1}(t) + (n+1)\gamma N_1 P_{n+1}(t) - [\gamma n N_1 + \gamma(n+1)N_2]P_n(t) \quad (4)$$

For steady state $\frac{\partial P_n}{\partial t} = 0$, and the steady state solution has the form

$$P_n^s = cq^n \quad (5)$$

Using the equation (1) and (2), we obtain

$$nN_2 + (n+1)N_1 q^2 - [nN_1 + (n+1)N_2]q = 0 \quad (6)$$

For $q = \frac{N_2}{N_1}$, we indeed have

$$nN_2 + (n+1)N_1 \left(\frac{N_2}{N_1}\right)^2 - [nN_1 + (n+1)N_2] \frac{N_2}{N_1} = 0 \quad (7)$$

The constant c can be determined by the condition that

$$\sum_{n=0}^{\infty} P_n^s = \frac{c}{1 - \frac{N_2}{N_1}} = 1 \quad (8)$$

and therefore

$$P_n^s = \left(1 - \frac{N_2}{N_1}\right) \left(\frac{N_2}{N_1}\right)^n \quad (9)$$

2. If the atoms are in thermal equilibrium, it follows from the Boltzmann statistics that $N_2/N_1 = e^{-\hbar\omega/k_B T}$. Then the steady state solution is

$$P_n^s = \left(1 - e^{-\hbar\omega/k_B T}\right) e^{-n\hbar\omega/k_B T} \quad (10)$$

Define $\beta = \frac{1}{k_B T}$, the average number of photons $\langle n \rangle$ in the steady state is given by

$$\begin{aligned} \langle n \rangle &= \sum_{n=0}^{\infty} n P_n^s \\ &= \left(1 - e^{-\beta\hbar\omega}\right) \frac{\partial}{\partial(-\beta\hbar\omega)} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \\ &= \frac{1}{e^{\beta\hbar\omega} - 1} \end{aligned} \quad (11)$$

which follows the Bose-Einstein statistics.

7.3 Solution: Master equation for a chemical reaction (Dimer formation)

1. —
2. —
3. —
4. The equation in hands

$$K_D(1 - z^2) \frac{d^2}{dz^2} G(z) + K_-(1 - z) \frac{d}{dz} G(z) - K_+(1 - z) G(z) = 0 \quad (12)$$

can be transformed to the modified Bessel equation by the appropriate change of variable and function. Correspondingly, the two linearly independent solutions of it are proportional to the modified Bessel functions of the 1-st and 2-nd kind (I and K)

$$G_1(z) = C_1(z+1)^{(1-2\beta)/2} \cdot I_{2\beta-1}[\sqrt{8\alpha(z+1)}],$$

$$G_2(z) = C_2(z+1)^{(1-2\beta)/2} \cdot K_{2\beta-1}[\sqrt{8\alpha(z+1)}].$$

In general, for the equation (12) there are *no* boundary conditions to select a unique solution. Instead, the choice between G_1 and G_2 can be made basing on a physical argument. The suggested argument is that in order to define a probability distribution $G(z)$ and all its derivatives should stay finite at $z = -1$. Indeed, e.g.

$$G(z)|_{z=-1} = \sum_{n=0}^{\infty} (-1)^n P_n \leq \sum_{n=0}^{\infty} P_n, \quad (13)$$

where the last sum is finite and equal to 1. Asymptotes for G_1 and G_2 as $z \rightarrow -1$ can be found from the definitions of I_n , K_n in terms of J_n and Taylor expansion for J_n , which can be looked up on Wikipedia.

$$G_1(z)|_{z \rightarrow -1} \sim \text{const},$$

$$G_2(z)|_{z \rightarrow -1} \sim (z+1)^{1-2\beta}.$$

We see that there is a problem with G_2 , since it, or one of its derivatives necessarily diverges as $z \rightarrow -1$ for any positive β . We conclude thus that $G(z) = C_1(z+1)^{(1-2\beta)/2} \cdot I_{2\beta-1}[\sqrt{8\alpha(z+1)}]$, where C_1 is found from the normalization condition $G(1) = 1$. For the numerical calculation of the averages and dispersions see the Mathematica sheet in the same folder. $\alpha = 0.1$, $\beta = 1$:

$$\langle n \rangle = \left. \frac{\partial G}{\partial z} \right|_{z=1} = 0.094,$$

$$\sigma = \sqrt{\langle n^2 \rangle - \langle n \rangle^2} = \left. \sqrt{\frac{\partial^2 G}{\partial z^2} + \frac{\partial G}{\partial z} - \left(\frac{\partial G}{\partial z} \right)^2} \right|_{z=1} = 0.30,$$

$\alpha = 1$, $\beta = 0.1$:

$$\langle n \rangle = 1.09,$$

$$\sigma = 0.89.$$

5. Relative fluctuations of n are small when $\langle n \rangle \gg 1$. This happens when the influx of monomers is sufficiently large compare to the loss, $K_+/K_- \gg 1$ and monomer formation rate $K_+/K_D \gg 1$.
6. In the assumed approximation the dimer formation term in Eq. ?? can be neglected and the solution is

$$G(z) = \exp\left(\frac{K_+}{K_-}(z-1)\right), \quad (14)$$

which results in relative fluctuations

$$\frac{\sigma}{\langle n \rangle} = \sqrt{\frac{K_-}{K_+}}. \quad (15)$$

So, for $\sigma/\langle n \rangle < 0.1$, one needs $K_-/K_+ < 0.01$.