Freie Universität Berlin
Fachbereich Physik
Prof. Dr. Roland Netz
http://www.physik.fu-berlin.de/en/einrichtungen/ag/ag-netz/lehre

22.01.2018
Due date: 29.01.2018

Advanced Statistical Physics II – Problem Sheet 12

Problem 1 – **Master equation**
Consider the three state model with transition rates k_i

$$A \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} B \underset{k_{CB}}{\overset{k_{BC}}{\rightleftharpoons}} C, \qquad A \underset{k_{CA}}{\overset{k_{AC}}{\rightleftharpoons}} C \tag{1}$$

a) (2P) Write down the master equation for the probability density $\vec{\rho}(t) := (\rho_A(t), \rho_B(t), \rho_C(t))^T$.

b) (2P) Find the stationary solution of the master equation for $k_{AC} = k_{CA} = 0$ and discuss it for the special case $k_{AB}/k_{BA} = k_{BC}/k_{CB}$.

c) (1P) Recall the definition of detailed balance

$$p(X)W(X \to Y) = p(Y)W(Y \to X). \tag{2}$$

$p(X)$ and $p(Y)$ are the probabilities of being in state X or Y respectively, and $W(Y \to X), W(X \to Y)$ are the transition probabilities (or transition rates) for going from one state to the other. Does the stationary solution of the previous example obey detailed balance?

d) (2P) Find the stationary solution for the case in which transitions can only happen in one "direction", i.e.

$$A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C, \qquad C \xrightarrow{k_{CA}} A. \tag{3}$$

Does detailed balance hold?

e) (1P) Discuss the special cases

- $k_{AB} = k_{BC} = k_{CA}$
- $k_{BC} = k_{CA}, \quad k_{AB} \to \infty$

for the stationary solution of the previous example.

f) (5P) Solve the master equation for the special case $k_{AB} = k_{BC} = k_{CA} = k$ and $k_{BA} = k_{CB} = k_{AC} = 0$ with initial condition $\vec{\rho}(0) = (1, 0, 0)$. *Hint:* Do a spectral decomposition of the rate matrix.

Problem 2 – **Reaction rate kinetics**
Consider the reaction

$$A + A \underset{k_1}{\overset{k_2}{\rightleftharpoons}} B + A \tag{4}$$

of two chemical substances A and B. The chemical kinetics equation for this reaction is:

$$\dot{y}(t) = k_2 x^2(t) - k_1 x(t) y(t) \tag{5}$$

Here, x and y are the concentrations of the two substances A and B, respectively.

a) (2P) Assume, that no particles can enter or leave the system, such that the sum of the masses of both substances is conserved. Show that in this case, there are two stationary states, y_1 and y_2, for the concentration of substance B.

b) (3P) Solve equation (5) for the initial condition $y(t = 0) = y_0$. *Hint:* First show, that (5) can be written as

$$\int_{y_0}^{y} \frac{d\tilde{y}}{(\tilde{y} - y_1)(\tilde{y} - y_2)} = (k_1 + k_2) \int_0^t d\tilde{t} \tag{6}$$

Result:

$$y(t) = y_2 + \frac{y_1 - y_2}{1 - \frac{y_0 - y_1}{y_0 - y_2} e^{t(y_1 - y_2)(k_1 + k_2)}} \tag{7}$$

c) (2P) Take the limit $t \to \infty$. For which initial values y_0 do you end up at the stationary state y_1 or y_2? What does this tell you about the stationary states y_1 and y_2?