Entrance Examination Physics and Chemistry of Biological Systems
September 2012

Solve **one** of the following problems (no extra credit is given for attempts to solve more than one problem). Write out solutions clearly and concisely. State each approximation used. Diagrams welcome. Number page, problem, and question clearly. All essays/solutions should be written in English. Do not write your name on the problem sheet, but use extra envelope.

Problem n. 1 – System of Langevin equations with harmonic spring

Consider the following system of uni-dimensional Langevin equations, describing the motion of two *identical* point particles 1 and 2 linked by a harmonic spring in a heat bath at temperature T:

$$\begin{aligned}\gamma\frac{d\,x_1(t)}{d\,t} &= -K\,(x_1(t)-x_2(t))+\xi_1(t)\\ \gamma\frac{d\,x_2(t)}{d\,t} &= -K\,(x_2(t)-x_1(t))+\xi_2(t).\end{aligned} \tag{1}$$

In Eq. 1:

- γ is the friction of the particles;
- K is the spring constant;
- $\xi_1(t)$ and $\xi_2(t)$ are stochastic forces acting on particle 1 and 2, respectively. They satisfy the thermal averages given by:
  1. $\langle \xi_1(t)\rangle = \langle \xi_2(t)\rangle = 0$;
  2. $\langle \xi_1(t)\,\xi_2(t')\rangle = 0$, and $\langle \xi_1(t)\,\xi_1(t')\rangle = \langle \xi_2(t)\,\xi_2(t')\rangle = 2\,\gamma\,\kappa_B\,T\,\delta(t-t')$, where κ_B is the Boltzmann constant and $\delta(t)$ is the Dirac delta function.

By introducing the two variables $y_1(t) = \frac{x_1(t)+x_2(t)}{2}$ and $y_2(t) = x_1(t) - x_2(t)$:

1. Show that the coupled system of Eq. 1 can be written as two *uncoupled* Langevin equations in the new variables y_1 and y_2.
2. Calculate the thermal averages $\Delta_1(t) \equiv \langle (y_1(t) - y_1(0))^2\rangle$ and $\Delta_2(t) \equiv \langle (y_2(t) - y_2(0))^2\rangle$.
3. Discuss shortly the short- and long-time behaviors of $\Delta_1(t)$ and $\Delta_2(t)$. In particular, show that $\lim_{t\to 0}\Delta_1(t) = 2D_1 t$ and $\lim_{t\to 0}\Delta_2(t) = 2D_2 t$, where $D_1 = \frac{1}{2}\frac{\kappa_B T}{\gamma}$ and $D_2 = 2\frac{\kappa_B T}{\gamma}$.

   Remembering that $\frac{\kappa_B T}{\gamma}$ equals the diffusion coefficient for particles 1 and 2, can we resort to simple physical arguments in order to deduce these results? Explain why.
4. Go back to the original variables x_1 and x_2 and show that the thermal average $\langle (x_1(t) - x_1(0))^2\rangle = \Delta_1(t) + \frac{1}{4}\Delta_2(t)$. Discuss the corresponding short- and long-time behaviors. Again, explain why they can be deduced by simple physical arguments.

Problem n. 2 – Maltus law vs Gompertz law

Consider the dynamical system

$$\frac{dx}{dt} = \gamma x, \qquad x \geqslant 0, \tag{2}$$

where $x(t)$ represents e.g. a population or the concentration of a substance, and γ is the rate

1. Describe what happens to $x(t)$ for $t \to \infty$ for the cases i) $\gamma > 0$; ii) $\gamma = 0$ and iii) $\gamma < 0$.

2. Assume now that γ is time-varying, $\gamma = \gamma(t)$, and that it obeys to the following law

$$\frac{d\gamma}{dt} = -\alpha\gamma, \qquad \alpha > 0, \tag{3}$$

   (a) what happens now to $x(t)$ for $t \to \infty$ in the case of $\gamma(0) > 0$?

   (b) can you obtain an explicit solution for $x(t)$?

3. Describe the qualitative differences between (2) with $\gamma = \text{const} > 0$ (Maltus law) and (2) with γ given by (3) (Gompertz law). In particular, which of the two is more suitable to describe the growth of a population in a confined space (e.g. a solid tumor) and why.

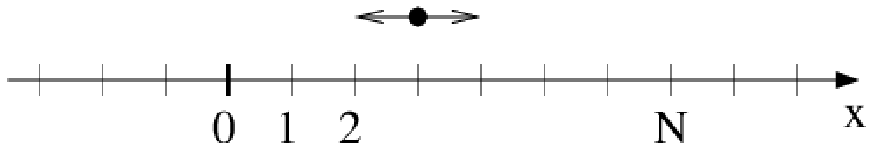
4. Compare the behavior of the combined system (2)-(3) with that of the following ODE

$$\frac{dx}{dt} = (-\alpha \ln(x))x \tag{4}$$

5. Discuss what happens to the growth rate in (4) in the case of small population (i.e., in the limit $x \to 0^+$). Is this the behavior you would expect for the growth of a very small population? Can you suggest a more realistic model?

Problem n. 3 – One-dimensional discrete random walk with absorbing boundaries

Consider a random walker on a one-dimensional regular lattice, as in the figure below.



At each time step, the walker moves randomly either the left or to the right. The two steps, in the $+$ or $-$ directions of the x axis are equiprobable.

- 1. Estimate the typical number of time steps required to the walker to reach a point at distance N from the origin.

From now on assume that the walker motion is restricted to the $[0, N]$ interval by the presence of two absorbing sites, located at $x = 0$ and $x = N$. In the walker reaches one of these two sites, then it is trapped and stays there forever.

- 2. Compute the probability that the walker starting at $x = 1$ will be eventually trapped at $x = N$.
- 3. Let us indicate with $s(x_0)$ the average number of steps required before a walker initially at x_0 is trapped at $x = N$. The average is intended taken over many walks all starting at x_0. Write down the relationships involving $s(x)$ for $x = 1, 2..., N$.
- 4. Provide an explicit expression for $s(1)$ as a function of N. *Hint: calculate explicitly* $s(1)$ *for very small values of* N *and inspect the obtained relationships*

Problem n. 4 – Electronic structure of molecules

According to Molecular Orbital Theory draw a sketch of the C_2, O_2, N_2 molecular orbital and comment on the bonding situation of these molecules.

Determine which molecule between C_2 and C_{2^-}, O_2 and O_{2^+} and N_2 and N_{2^+} has the greater dissociation energy and explain why.

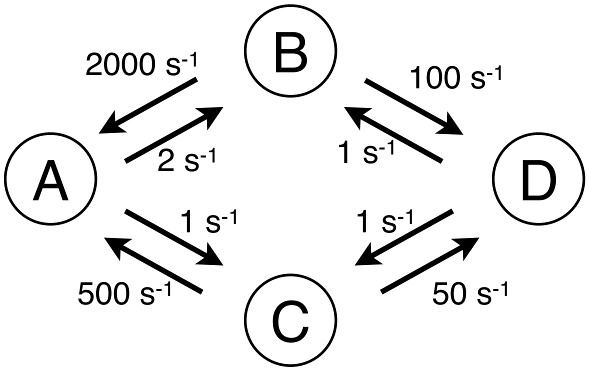
Write the electronic configuration and determine the ground state symbols for C_2 and C_{2^-}, O_2, N_2, N_{2^+}, O_{2^+}.

Considering the Hueckel Molecular Orbital Theory determine the energy level diagram of the ethene and draw a picture of the molecular orbital.

Which similarities/differences would you expect between the bonding properties of ethane and of an oxygen molecule?

Can oxygen and ethene be coordination ligands of transition metal? Describe qualitatively how they can bind to a generic transition metal.

Problem n. 5 – Equilibrium and steady state in a 4-state model



A system has four metastable states labeled as A, B, C and D. The possible transitions among these states are shown in Figure, where also the corresponding rates are indicated. At equilibrium:

- Which is the most stable among the 4 states? Which state is more stable among B and C?
- Find the equilibrium probability for each of the 4 states.
- Consider the two possible reaction pathways connecting D and A, namely the sequences ($D \rightarrow B \rightarrow A$) and ($D \rightarrow C \rightarrow A$). Which is the most likely to be observed?
- Compute the relative probability of the two pathways considered in the last point.

Consider now an additional transition $A \rightarrow D$ with rate equal to k.

- Is the system able to reach equilibrium? Is the system able to reach a steady state?
- In the two limiting cases $k \rightarrow 0$ and $k \rightarrow \infty$, compute the power dissipated as a function of k