PhD Entrance Examination
Physics and Chemistry of Biological Systems
June 2015

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 – Mean first hitting time in d dimensions

Consider a random-walker on the $\overbrace{L \times L \times L \times ... \times L}^{d}$ d-dimensional cubic lattice of linear size L starting from a random position on the lattice. Reflecting boundary conditions are assumed at the border of the lattice.

For each walk, let n be the number of steps needed by the walker to reach an absorbing *target* site located at the origin of the lattice, and $\langle n \rangle$ be its mean value.

By employing scaling arguments:

1. Discuss how $\langle n \rangle$ depends on L and on the lattice dimension d. *Hint.* It might be useful to discuss first the behaviour of the "density" of explored sites, $\rho(m) \equiv \frac{m}{r(m)^d}$, where $r(m)$ is the average displacement of the walker after m steps.

2. Generalize the discussion by considering a generic walker with average displacement $r(m) \sim m^\gamma$ $(0 < \gamma < 1)$.

3. Assume now, that the same walker obeying $r(m) \sim m^\gamma$ is diffusing on a fractal lattice of fractal dimension d_f, *i.e.* the total number of lattice sites $\mathcal{N}$ included in a sphere of radius $\mathcal{R}$ scales as $\mathcal{N} \sim \mathcal{R}^{d_f}$. Again, the single absorbing (target) site in the lattice defines the origin of the latter. How do you think that $\langle n \rangle$ now depends on γ and d_f?

Problem n. 2 – A flexible chain under tension

Consider a fully-flexible polymer chain of N segments of length b, $\{\vec{b}_1, \vec{b}_2, ..., \vec{b}_N\}$, in canonical equilibrium at temperature T. The chain is embedded in a three-dimensional space and has no excluded volume. A force $\vec{f}$ is applied to the two termini to pull them apart.

1. Write down the partition function of the chain.

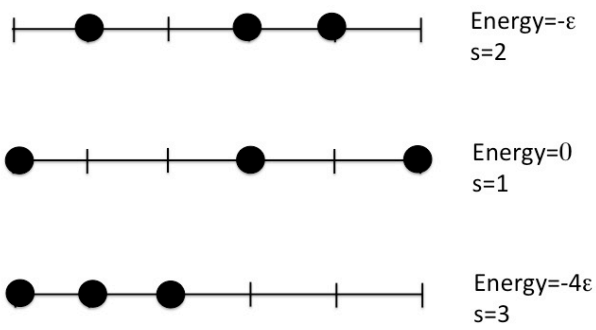
2. At low applied forces the chain behaves like a Hookean spring. By simply inspecting the expression for the partition function, i.e. without doing further calculations, discuss how such spring constant depends on temperature. Comment your result.

3. Now derive, via an explicit calculation, the relationship between the chain end-to-end separation (the so-called extension) and the applied force. Sketch the force extension curve and comment your result.

4. Consider the end-to-end distance of the chain $\vec{R}_{ee} \equiv \sum_i \vec{b}_i$ and provide an expression for how its modulus depends on the applied tension, $f \equiv |\vec{f}|$. Derive, to leading order in f, how R_{ee} depends on f in the low-force limit.
   Compare the expression with the force-extension relationship that you derived previously and comment your result.

Problem n. 3 – A simple model of condensation.

Consider three particles on a one dimensional lattice with n sites. The particles cannot occupy the same site. If two particles occupy neighbouring sites they interact with an energy $-\varepsilon$. If the three particles occupy three neighbouring sites, their energy is -4ε. Some examples of the possible configurations of the system for $n = 6$ are depicted in figure.



- For $n = 5$ compute the average energy as a function of the temperature T assuming the system is in canonical equilibrium. Plot a graph illustrating the beahviour of this quantity.
- For $n = 5$ compute the entropy of the system as a function of T.

The three particles can form a cluster of size $s = 3$ if they occupy three neighbouring sites, of size $s = 2$ if two of them occupy two neighbouring sites and size $s = 1$ otherwise.

- Now take $T = 1$, $n = 6$ and compute the probabilities P_s of observing a cluster of size s as a function of ε. For which value of ε is the "condensed state" $s = 3$ equally probable of the "disordered state" $s = 1$?
- Find the minimum value of n for which the condensed state and the disordered state can be separated by a barrier, namely for which it exists a value of ε for which $P_2 < P_1$ and $P_2 < P_3$

Problem n. 4

Hemoglobin is an iron containing protein in charge of carrying molecular oxygen from respiratory organs to the rest of the body. The protein contains 4 heme groups (Figure) each reversibly binding one molecule of oxygen.
CO binds to heme group more strongly than O_2, and its (fairly irreversible) binding hampers hemoglobin from carrying out its normal function as molecular oxygen carrier. Because of this strong affinity towards hemoglobin CO is very toxic.

1) Draw the molecular orbital energy diagram for CO and O_2 and explain similarity and differences in their electronic structures

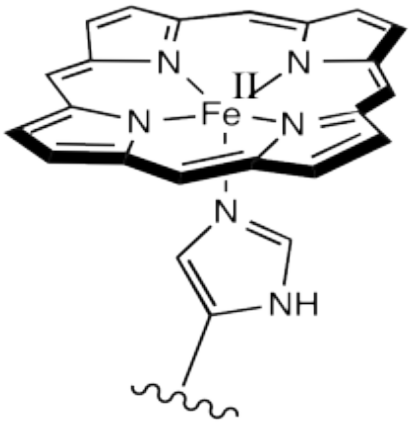
2) Draw the splitting of the Fe d orbitals relative to the Fe-porhyrin complex according to crystal field theory.

3) Draw the molecular orbital energy levels for the binding of CO and O_2 to the iron-porphyrin of hemoglobin.

4) Sketch the structure of the resulting complexes and the possible resonant states, focusing on the Fe-O_2 moiety

5) Guess the spin state of the resulting complexes.

6) On the basis of the MO diagram are can you to explain why CO binds more strongly than O_2 to Fe-porphyrin?



Electronic configuration of Fe is [Ar] 3d6 4s2
Electronic configuration of C [He] 2s2 2p2
Electronic configuration of O [He] 2s2 2p4