PhD Entrance Examination
Physics and Chemistry of Biological Systems
June 2016

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 – A toy model for a polymer chain across the θ-point

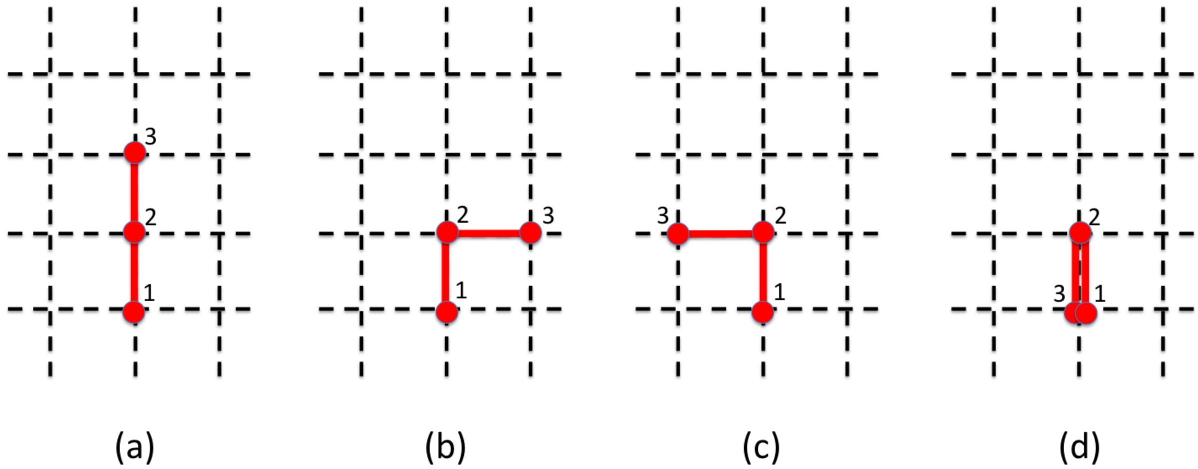


Figure 1: *(a)* Straight line; *(b, c)* Kinked conformations; *(d)* Back-folded conformation.

A model polymer chain with 2 bonds and 3 nodes on the 2-dimensional square lattice has 4 possible conformations (solid lines, Fig. 1), with possible energies: $E(a) = 0$, $E(b) = E(c) = -\epsilon_s$, $E(d) = -2\epsilon_s + \epsilon_a$, with $\epsilon_s, \epsilon_a \geq 0$. ϵ_s describes the bending penalty, while ϵ_a models an attractive interaction between nodes 1 and 3 when they occupy the same lattice site. The polymer is at equilibrium in a thermal bath with temperature T.

Part 1. Assume $\epsilon_s = 0$ and $\epsilon_a > 0$. Calculate:

1. The partition function $\mathcal{Z}$ of the system.
2. The average polymer span $\sqrt{\langle R^2 \rangle}$, where $\langle R^2 \rangle$ is the mean-square spatial distance between monomers 1 and 3. Sketch a plot of $\sqrt{\langle R^2 \rangle}$ as a function of T and comment briefly.
3. The temperature T_θ corresponding to the transition where conformation (d) has the largest occupation.

Part 2. Assume $\epsilon_s > 0$ and $\epsilon_a = 0$. Again, calculate $\mathcal{Z}$ and $\sqrt{\langle R^2 \rangle}$, sketch a plot of the latter as a function of T and comment briefly.

Part 3. Assume now $\epsilon_s, \epsilon_a > 0$. For which values of these two parameters does it exist a physical (*i.e.*, finite) value of T_θ? Again, comment briefly.

Problem n. 2 – A chain of springs

Consider a long chain of N beads connected by harmonic springs, of spring constant k, embedded in a three-dimensional space. The beads are phantom (no excluded volume interactions) and the chain is in canonical equilibrium at temperature T.

- Compute the average distance of the beads from the chain center of mass.
- Compute the most probable end-to-end distance of the chain.
- What force is necessary to apply to keep the ends at a given distance, $\vec{R}$?
- Consider now a chain whose ends are strictly constrained at distance $\vec{R}$ while the rest of the chain is unconstrained. Without loss of generality assume that $\vec{R}$ is along the x Cartesian axis. What is the typical distance of the chain midpoint (i.e. bead $N/2$) from the x axis? What conclusions can you draw about the chain properties?

Problem n. 3 – Out of equilibrium harmonic system

A particle of mass m moves in one dimension following an overdamped equation at zero temperature subject to a moving spring of stiffness k

$$\dot{x}(t) = -\frac{k}{\gamma m}(x(t) - \bar{x}(t))$$

Here x is the position of the particle, t is the time, $\dot{x}$ indicate the velocity of the particle, $\bar{x}(t)$ is an arbitrary law indicating how the center of the spring is moving with time, and γ is a friction coefficient. At time $t = 0$ the particle is located in the origin ($x = 0$). The candidate is asked to answer to the following questions:

1. Assuming $\bar{x}(t) = x_0$ (spring center is fixed), find an explicit expression for the trajectory $x(t)$.
2. Assuming $\bar{x}(t) = x_0 + v_0 t$ (spring center is moving at constant velocity v_0), find an expression for $x(t)$ valid in the asymptotic limit $t \to \infty$. How much power is dissipated to maintain the center of the spring moving at constant velocity? Discuss how the dissipated power depends on k, γ, m, and v_0.
3. In the same conditions as in the previous point, find an exact expression for the trajectory $x(t)$. How much energy is dissipated as a function of time?
4. Compare the results of point 2 and 3. Discuss in which cases the approximation used for point 2 is correct.
5. Now assume that N particles are connected by springs such that the first particle is connected to the center of the spring located in $\bar{x}(t)$ and each particle is connected to the following one:

$$\dot{x}_1(t) = -\frac{k}{\gamma m}(x_1(t) - \bar{x}(t)) - \frac{k}{\gamma m}(x_1(t) - x_2(t))$$

$$\dot{x}_2(t) = -\frac{k}{\gamma m}(x_2(t) - x_1(t)) - \frac{k}{\gamma m}(x_2(t) - x_3(t))$$

$$\cdots$$

$$\dot{x}_{N-1} = -\frac{k}{\gamma m}(x_{N-1}(t) - x_{N-2}(t)) - \frac{k}{\gamma m}(x_{N-1}(t) - x_N(t))$$

$$\dot{x}_N = -\frac{k}{\gamma m}(x_N(t) - x_{N-1}(t))$$

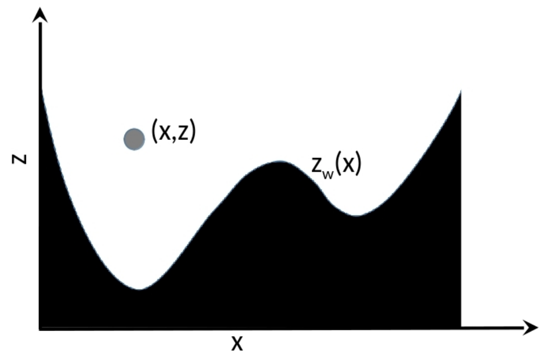
   Assume the center of the spring is moving at constant velocity v_0. How much power is dissipated to maintain the center of the spring moving at constant velocity?
6. Discuss qualitatively how do you expect the results to be affected if the system is kept in contact with a thermal bath at temperature T.

Problem n. 4 – Two particles in a gravitational field

Consider a particle of coordinates (x, z) and mass m in a gravitational field gz, acting in the z direction (g is the gravitational constant). The particle is confined along z by a wall of equation

$$z_w(x) = 3x^4 + 4x^3 - 12x^2$$

Therefore, the particle can occupy only points of coordinates (x, z) with $z > z_w(x)$ (see figure).



- Compute the free energy of the particle as a function of x at a temperature T
- Compute the approximate value of the relative probability of observing the particle at $x < 0$ and at $x > 0$. Hint: perform a Taylor expansion of the free energy in the neighbourhood of the free energy minima. Discuss the scaling of the relative probability as a function of T and of the mass of the particle.
- Take now $\frac{mg}{k_B T} = 1$. Draw an approximate graph of $P(z)$, the probability of observing the particle at a height z. Discuss its shape. Is $P(z)$ continuous? Is $P(z)$ differentiable?

Consider now a second particle, of coordinates (x', z'). The two particles interact with a hard-sphere repulsive potential

$$V(|x - x'|) = \begin{cases} \infty & \text{if } |x - x'| < l \\ 0 & \text{otherwise} \end{cases}$$

- Assuming that l is very small, compute the free energy of the first particle as a function of x at a temperature T.

Problem n. 5 – Chemical equilibrium of metal ions

Ammonia and Ag^+ ions in water solution leads to the formation of coordination complexes with the following equilibrium constants: $Kf_1 = 2 \times 10^3$, $Kf_2 = 8 \times 10^3$.

Describe the bonding situation of an ammonia molecule according to molecular orbital theory.

Considering a $[NH_3] = 1 \times 10^{-2}$M, which is the most abundant complex (formed by NH_3 and Ag^+) present in solution.

Draw the structure of the most abundant complex in solution structure, describe and explain the bonding situation of the most abundant complex.

If a weak acid is added to the solution how do you expect the equilibrium of formation for the different coordination complexes to be affected?