PhD Entrance Examination
Physics and Chemistry of Biological Systems
March 2018

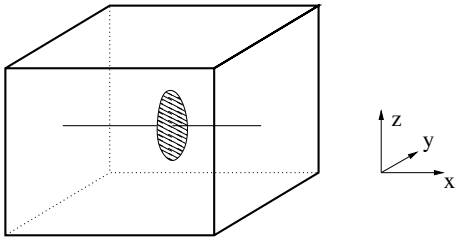
Solve **one** of the following problems (no extra credit is given for attempts to solve more than one problem). Write out solutions clearly and concisely. State each approximation used. Diagrams welcome. Number page, problem, and question clearly. All essays/solutions should be written in English. Do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

Problem n. 1 – Particles in a box with a sliding plate

Consider a monodispersed collection of N particles of diameter σ and mass m in canonical equilibrium at temperature T in a cubic box of side L. Assume, for simplicity, that the interactions between the particles are negligible.

1. Compute the partition function for the system and show that, to leading order, it is proportional to $(\frac{L-\sigma}{\lambda})^{3N}$, where λ is a characteristic lengthscale of the system.

Inside the box we now add a circular plate of radius R, with $\sigma << R << L$, that can freely slide along a rail – the rail is parallel to the x Cartesian axis – with its face always perpendicular to the x axis, see Figure. Assume, for simplicity, that plate is infinitely thin and that the interactions of the particles with the rail are negligible. The plate, however, is impenetrable to the particles.



2. Write the expression for the partition function of the system for a generic position of the plate along the rail, x.

3. Write the expression for the probability that the plate is at position x, draw a sketch of it, and give a physical interpretation of the result.

4. Write the expression for the pressure exerted by the particles on the plate when the latter is at position x and, making the necessary approximations, discuss and explain its dependence on T, N, V, σ and m.

Problem n. 2 – One-dimensional absorbed polymer chain

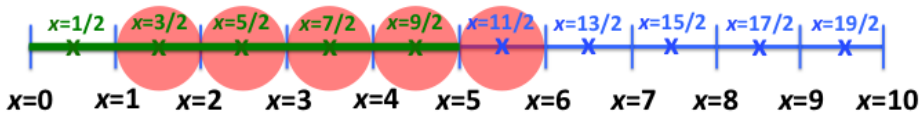


Figure 1: Rigid polymer rod of $N = 5$ chemical units on the one-dimensional lattice of linear extension $2N = 10$ lattice sites. The polymer may interact with the green portion of the lattice.

Consider a linear polymer chain composed of N chemical units ("monomers"), confined on the one-dimensional lattice with sites coordinates "$i - 1/2$" ($i = 1, 2, ..., 2N$). The polymer is taken initially as a rigid rod. Monomers interact with lattice sites $i = 1, ..., N$ with energy $-|\epsilon| < 0$ and with the other sites with energy $= 0$.

(a) Calculate the free energy $\mathcal{F}(N, T)$ of the system. In the limit $N \to \infty$ sketch a picture of $\mathcal{F}$ as a function of T.

(b) Repeat the same for the average internal energy $\mathcal{E} = \mathcal{E}(N, T)$ of the system.

Suppose now that the part of the chain which is not interacting with the left part of the lattice is no longer a rigid rod and folds as a one-dimensional random-walk. Assuming no interactions between this part of the chain and the left part of the lattice:

(c) Derive the critical temperature T_c above which the random-walk state dominates over the absorbed state.

(d) Repeat points (a) and (b) above for this system.

Problem n. 3 – Partition function of a protein

A protein can be in $N+2$ different states, one of which is folded, another one which is an intermediate state, and the other N which are unfolded. The folded state has energy equal to ϵ_F, the intermediate state has energy equal to ϵ_I, and each unfolded state has energy equal to ϵ_U, with $\epsilon_I > \epsilon_U > \epsilon_F$. The protein is at equilibrium at temperature T.

- Find the probability that the protein is in the folded state at temperature $T = 0$.
- Find the probability that the protein is in the folded state in the limit of large temperature, $T \gg \frac{\epsilon_U - \epsilon_F}{k_B}$, where k_B is the Boltzmann constant.
- Find the temperature T at which the population of the intermediate state is maximized.
- Make three sketches showing the probability of finding the protein in the folded, in the intermediate, or in any one of the unfolded states as a function of the temperature.

The melting temperature, T_m, is defined as the temperature at which the probability of the protein to be folded is equal to the probability of the protein to be unfolded.

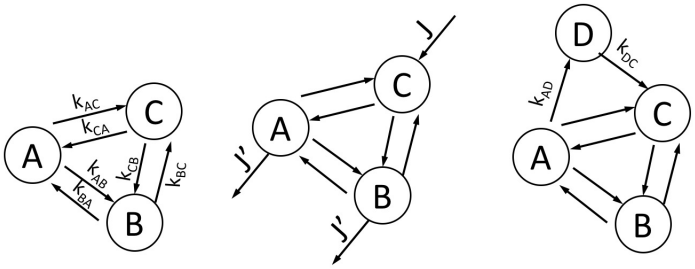
- How does T_m depend on ϵ_U, ϵ_F, ϵ_I and N?

The gyration radius of the protein in the folded, intermediate, and unfolded states is respectively $R_F = 1\text{nm}$, $R_I = 1.2\text{nm}$, and $R_U = 2\text{nm}$. An experimental measurement reports that the average value of the gyration radius is 1.2nm.

- Assuming the $\epsilon_I - \epsilon_U \gg k_B T$, compute the population of the unfolded, intermediate, and folded state.
- Within the same assumption, and also knowing that $\epsilon_U - \epsilon_F = 5 k_B T$, estimate the number of unfolded states N.

Problem n. 4 – A rate model for a particle

Consider a particle that can exist in the three states A, B and C (see Figure, left panel). The possible transitions among these states are shown in the Figure. The rates are the following: $k_{AB} = 4\kappa$, $k_{BA} = 2\kappa$, $k_{AC} = 8\kappa$, $k_{CA} = 2\kappa$, $k_{BC} = 6\kappa$ and 3κ where κ has the dimension of an inverse time.



- Compute the equilibrim probability of observing the particle in the three states. Does the result depend on the value of κ?

Assume now that new particles are created in state C with a current J and particles are removed from state B and state A with an identical current J' (see figure, central panel).

- For which value of J' is the system able to reach a steady state?
- Compute the steady state probability of the three states in this new condition. Does the result depend on the value of κ?
- Compute the steady state current between state C and A.

Consider now an additional state D, and take $J = J' = 0$. The possible transitions involving this states are shown in the right panel. The rates involving the new state are $k_{AD} = 4\kappa$ and $k_{DC} = \kappa$,

- Is the system able to reach equilibrium? Is the system able to reach a steady state?
- Compute the steady state current between state C and A.

Chemistry Exercise Spring 2018

Consider the NO_2 radicalic molecule [N: $1S^2 2S^2 2p^3$; O: $1s^2 2s^2 2p^4$]

(a) Determine its molecular geometry considering that the unpaired electron occupies a non-hybrid atomic orbital. Describe the molecular orbitals and write the possible resonance structures of the molecule.
(b) Determine its molecular geometry considering that the unpaired electron occupies a hybrid orbital. Describe the molecular orbitals and write the possible resonance structures of the molecule.
(c) Which of the two geometries predicts the molecule to be paramagnetic?
(d) Which of the two geometries predicts the molecule to be polar?
(e) Considering the inter electronic repulsion, which of the two geometries is the most energetically favored?
(f) Due to its radicalic nature the NO_2 molecule is very reactive and can dimerize. Predict the molecular geometry of its dimer.
(g) How would the geometry of the molecule change upon addition and removal of one electron?