PhD Entrance Examination
Physics and Chemistry of Biological Systems
June 2017

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 – Fractal model for polymer chains

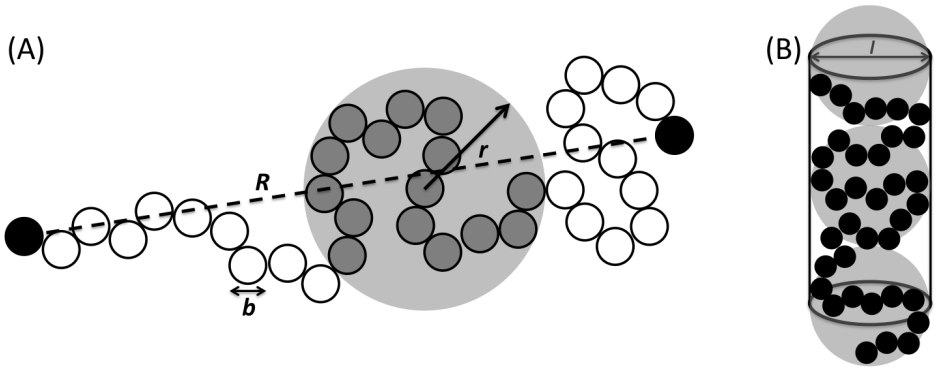


Figure 1: (A) Model for a free polymer chain made of N monomers of linear size b. The polymer average size is R. The monomers contained inside a sphere of radius r (light gray) centered on an arbitrary chosen monomer along the chain are colored in dark gray. End monomers are colored in black, for clarity. (B) The same polymer (black circles) confined to a cylindrical container with cross-section $b \ll l \ll R$.

A single, free polymer chain (Fig. 1(A)) in $d = 3$ dimensions can be modeled as a self-similar (fractal) object of fractal dimension d_f, *i.e.* the average number of monomers $n(r)$ inside a sphere of radius r centered on any of the monomers of the chain scales as $n(r) \sim \left(\frac{r}{b}\right)^{d_f}$, where b is the monomer size. Monomers repel each other because of exclude volume effects. N and R are the *total* number of monomers and polymer size, respectively.

Solve the following questions:

[1] Physics imposes lower (d_l) and upper (d_u) bounds to d_f (*i.e.*, $d_l \leq d_f \leq d_u$). Which ones?

[2] Calculate the scaling behavior of the monomer-monomer radial distribution function, $g(r)$, which is defined as the average monomer density at spatial distance r from any chosen monomer. Discuss the result at the light of point (1).

[3] Generalize points (1) and (2) to a polymer chain of fractal dimension d_f in d dimensions.

For the remaining questions, assume again $d = 3$.

[4] Confine the polymer to a cylindrical container with cross-section of linear size ℓ satisfying $b \ll \ell \ll R$ (Fig. 1(B)). Polymers are soft objects, the chain rearranges its shape in order to fit inside the cylinder[1], and it can be described as a linear array of non-overlapping blob-like regions (in gray in Fig. 1(B)) of diameter ℓ.

By adopting only scaling arguments:

[a] Which is the average number of monomers, n_ℓ, fitting inside a spherical blob?

[b] How does it scale the *total* number of blobs, n_b, with n_ℓ and N? And the polymer extension along the axis of the cylinder? Justify your answers, and verify the results in the two limits of $\ell \to b$ and $\ell \to R$.

[1] The container is supposed to be long enough to accomodate the entire polymer.

Problem n. 2 – Transfer matrix application to a Potts model

In this problem you are asked to use the transfer matrix technique to characterize the canonical properties of a one-dimensional chain of N spins, σ, with periodic boundary conditions (i.e. $\sigma_{N+1} \equiv \sigma_1$). The chain is in thermal equilibrium at temperature T.

Consider first a chain of Ising spins, $\sigma_i = \{-1, +1\}$, with nearest neighbour interactions and subject to an external field, H. The Hamiltonian is:

$$\mathcal{H} = -J \sum_i \sigma_i \sigma_{i+1} - H \sum_i \sigma_i \ , \tag{1}$$

with $J > 0$.

1. Write down the exact expression for the partition function. Provide the limiting free energy per spin in the limit $N \to \infty$.
2. Compute the canonical expectation value of the magnetization per spin, $\langle \sigma_i \rangle$ in the limit $N \to \infty$.
3 Considering the result at point 2., can you give a physical interpretation to the components of the largest eigenvector of the transfer matrix?

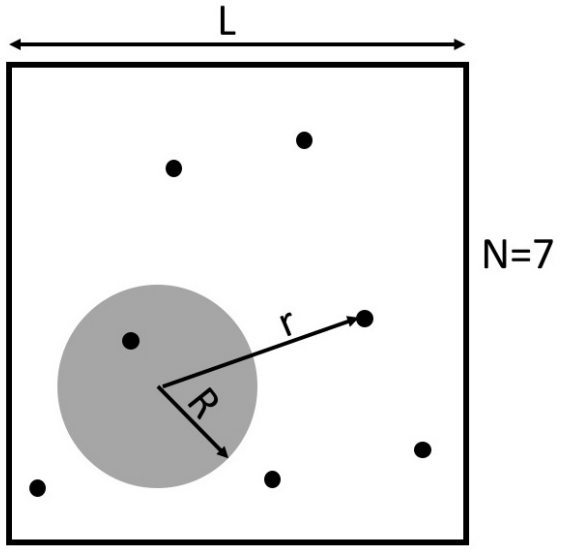
Consider now a chain of spins that can be in one of three discrete states, $\sigma_i = \{-1, 0, +1\}$, with nearest neighbour interactions and in zero external field. The nearest-neighbour interactions are favourable only for identical neighbouring spins and zero otherwise. The Hamiltonian is:

$$\mathcal{H} = -J \sum_i \delta_{\sigma_i, \sigma_{i+1}} \ . \tag{2}$$

4. Compute the exact partition function of the system. Provide the limiting free energy per spin in the limit $N \to \infty$.
5. Using the observations at point 3, or your physical insight, discuss how the results would generalize for a system still described by Hamiltonian (2) but where the spins can be in one of p discrete states, where p is a generic integer number.

Problem n. 3 – Equilibrium properties of a mixture of particles

Consider a particle of radius R inside a square box of side L. The particle cannot get closer than R from the box wall. We assume $R < L$. The same box contains also N particles of negligibly small radius (see figure).



The small particles do not interact with each other, but interact with the large particle with a potential $V(r)$ depending only on their distance r from the center of the large particle:

$$V(r) = \begin{cases} w & \text{if } r < R \\ 0 & \text{otherwise} \end{cases}$$

The system is in canonical equilibrium at a temperature T

1. For $N = 1$ compute the probability to observe the small particle within a distance R from the center of the large particle.
2. Plot a graph illustrating the behavior of this quantity, considering two cases: $w < 0$ and $w > 0$.
3. Compute the partition function of the system for a generic value of N.
4. Compute the pressure exerted by the particles on the box walls (hint: the pressure can be estimated as a suitable logarithmic derivative of the partition function)
5. Compute the pressure in the limiting case $w \to -\infty$ and provide a physical interpretation of the result.

Problem n. 4 – A gas of reactive particles

Consider a box of volume V containing N_A particles of type A and N_B particles of type B. Particles are not interacting and are at equilibrium.

1. Given a particle i of type A, compute the probability that a chosen particle j of type B is within a distance d from particle i. You can ignore boundary effects, but you should not make any further assumption on the values of d, V, N_A, and N_B.

2. Given a particle i of type A, compute the probability that there is *at least one particle* of type B within a distance d from particle i.

3. Now consider the same system in the thermodynamic limit ($\lim_{N_A\to\infty} \frac{N_A}{V} = \rho_A$ and $\lim_{N_B\to\infty} \frac{N_B}{V} = \rho_B$). How does the probability to find *at least one particle* of type B within a distance d from particle i depends on d, ρ_A, and ρ_B?

4. Now assume that when two particles of type A and B are closer than d they convert irreversibly to a single particle of type C with probability per unit time $k_{A+B\to C}$. Assume to be in the limit in which $d^3\rho_B \ll 1$. Discuss the time evolution of ρ_A, ρ_B, and ρ_C addressing to the following issues:

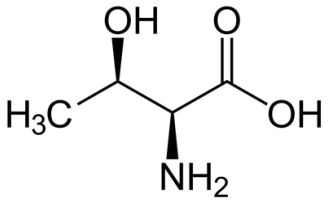
   - Which is the value of ρ_A, ρ_B, and ρ_C in the limit of $t \to \infty$?
   - Draw a figure showing the approximate behavior of $\rho_A(t)$, $\rho_B(t)$, and $\rho_C(t)$.
   - If at the beginning of the experiment $\rho_A = \rho_B = \rho_0$ and $\rho_C = 0$ find the analytical expressions for $\rho_A(t)$, $\rho_B(t)$, and $\rho_C(t)$.

Problem n 5 - Electronic Structure of Allyl Moiety

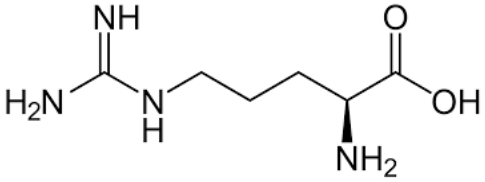
1. Determine and discuss the molecular orbitals and the structure of the allyl cation $CH_2CHCH_2^+$

2. Determine and discuss the energy level diagram of the allyl cation and anion according to the Hückel theory and calculate the resonance energy of the two molecules.

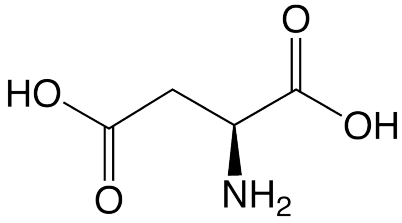
3. Consider the following aminoacids and establish:
   Which is the protonation state of the side chains at physiological pH?
   Which side chain has a resonant structure similar to the allyl cation or anion at physiological pH?
   Which side chain has a chiral center?



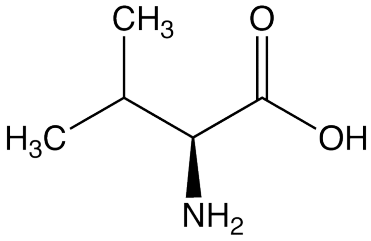
Threonine



Arginine pKa (side chain) 12.48



Aspartate pKa side chain 8.37



Valine