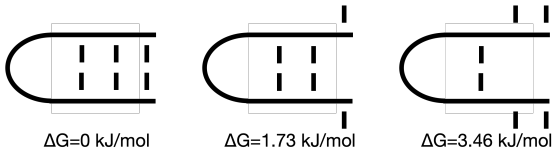
PhD Entrance Examination
Physics and Chemistry of Biological Systems
March 2021

IMPORTANT GUIDELINES

- Solve **three** of the following problems.
- No extra credit is given for attempts to solve more than three problems.
- Do not write your name on the problem sheet nor use any mark that can identify you, as this would invalidate your exam.
- 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.

Exercise 1



A RNA molecule can exist in one of the three states as depicted in the figure. The relative energy of each state is equal to the number of broken Watson-Crick pairs multiplied by 1.73 kJ/mol, as indicated. Assuming the system at equilibrium at temperature T=300 K, and given k_B=0.00831 kJ/mol/K, compute the probability of observing each of the three states and the average number of broken Watson-Crick pairs. Then consider the limiting case of an infinitely long molecule, where an arbitrary number of consecutive Watson-Crick pairs starting at the terminal can be broken. Compute the average number of broken Watson-Crick pairs in this case.

Exercise 2

Consider N non-interacting classical identical particles in the *microcanonical* ensemble, with single-particle Hamiltonian given by the expression:

$$\mathcal{H} = \frac{\vec{p}_i^{\,2}}{2m} + c|\vec{q}_i|^\alpha \,,$$

where $\vec{p}_i$ and $\vec{q}_i$ are the momentum and the position of the i-th particle, m is the mass, $c > 0$ is a prefactor and α is a real exponent. The total energy of the system is E.

By neglecting numerical prefactors:

1. Derive the expression $\Gamma = \Gamma(m, c, \alpha, N, E)$ for the volume of the phase space occupied by the N particles.

2. Derive the corresponding entropy $\mathcal{S}$ of the system and the temperature T. For temperature T to be > 0, what is the lower bound for α?

3. Does the formula for T derived at point (2) match the classical textbook expression for $\alpha = 2$?

Exercise 3

A system undergoing a chemical reaction is prepared in a state A. The residence time t in this state is exponentially distributed, namely $t \sim \text{Exp}(\tau)$ with $\tau = 1$ ns. What is the probability of observing a reaction within the first 2 ps? What is the probability that the system is still in state A after 10 ns? What is the expected value and the standard deviation of the residence time?

Exercise 4

Common experience tells us that oil doesn't mix with water while table salt mixes with water. In this question, you will explore some of the physical chemistry concepts underlying these phenomena.

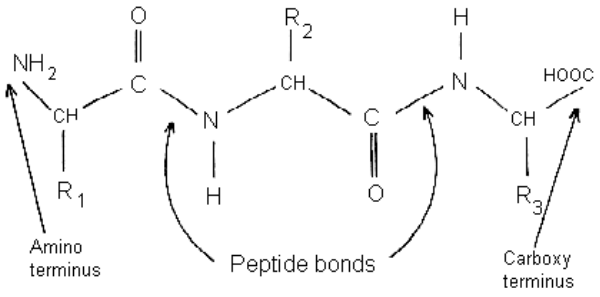
1. Consider two oily molecules such as methane or if you prefer, two argon atoms, interacting with each other. What types of interaction forces exist between the two molecules or atoms? Make a sketch of the interaction potential between the two molecules/atoms as a function of the distance r between them.

2. Now instead, consider two ions, a sodium (Na+) and chloride ion (Cl-) interacting with each other. What types of forces exist between these two ions? Make a sketch of the interaction potential between Na+ and Cl- as a function of the distance r between them and overlap it with the sketch in the previous question.

3. If the two ions Na+ and Cl- interact with each other in a liquid like water, how do you expect the interactions to change, if at all. How about two oily methane molecules or argon atoms interacting in water? In light of your observations made in this problem, why don't oil and water mix?

Exercise 5

Consider the following tripeptide:



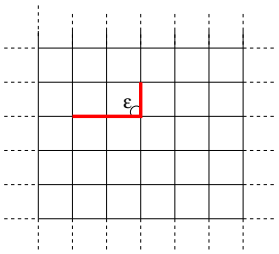
1. Which chemical reaction gives the formation of the peptide bonds?

2. The four atoms O C N H involved in the peptide bonds are found to be in a planar arrangement. Why? What can be said about the length of the CN peptide bond?

3. Describe qualitatively the energetic profile relative to the rotation around the CN peptide bond.

4. In water solution, the "Amino terminus" and "Carboxy terminus" moieties are sensitive to the pH. What happens to them changing the pH of the solution?

Exercise 6



Consider the ensemble of isolated walks of three steps on an infinitely extended square lattice. The walks are self-avoiding, in that they cannot retrace themselves, and there is an energy penalty $\epsilon > 0$ for each bend in the walk, see Figure. Assume that the system is in canonical equilibrium at temperature T.

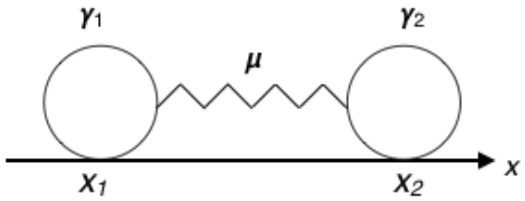
Using the symmetries of the lattice,

1. write an expression for the probability that the walks are fully extended (no bends), sketch its dependence on temperature, and discuss the limits $T \to 0$ and $T \to \infty$,

2. write an expression for the average number of bends in a walk, $\langle n_b \rangle$, sketch its dependence on T and discuss the same limits as above,

3. write an expression for the variance of the number of bends, $\sigma^2_{n_b} = \langle (n_b - \langle n_b \rangle)^2 \rangle$.

Exercise 7



Consider a dimer particle in 1-d as shown in the figure. The two (point) particles are connected to each other via a harmonic spring of zero rest length and spring constant μ. The positions of the two particles are denoted by x_1 and x_2 and their friction coefficients by γ_1 and γ_2. The system is maintained at a temperature T. The (coupled) equations of motion for the two particles can be written as

$$\frac{dx_1}{dt} = -\frac{\mu(x_1 - x_2)}{\gamma_1} + \sqrt{\frac{2k_B T}{\gamma_1}}\chi_1, \tag{1}$$

$$\frac{dx_2}{dt} = -\frac{\mu(x_2 - x_1)}{\gamma_2} + \sqrt{\frac{2k_BT}{\gamma_2}}\chi_2, \tag{2}$$

where χ_1 and χ_2 are independent white Gaussian noise processes with zero mean and Dirac-delta variance ($\langle\chi(t)\chi(t')\rangle = \delta(t - t')$). From the above equations obtain the equations of motion for the 'inner coordinate' $x = x_1 - x_2$ and the 'collective coordinate' $X = (\gamma_1 x_1 + \gamma_2 x_2)/(\gamma_1 + \gamma_2)$. In this new coordinate system, are the two equations coupled? Obtain the mean-squared-displacement $\langle X^2(t)\rangle$ for the initial condition $X(t = 0) = 0$. Show that for the special case of $\gamma_1 = \gamma_2 = \gamma$, for which X becomes the center of mass coordinate, it diffuses with a diffusion coefficient $\frac{k_BT}{2\gamma}$