PhD Entrance Examination
Physics and Chemistry of Biological Systems
April 2024

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, using English language only.
- Number page, problem, and question clearly.
- Text and solutions will be screened to detect use of generative AI, which is not admitted.

Exercise 1

In an experiment of microcalorimetry one studies a polymer chain made of N alanines. Each alanine can either be in a state of length a with energy 0 or length ka with energy $\epsilon > 0$. The polymer is in equilibrium in a aqueous solution at temperature T.

1. Predict the heat capacity of the polymer.

2. Is there any phase transition as a function of the temperature? Why?

3. If the experiment reports that the energy fluctuations of the system obey $\langle E^2\rangle - \langle E\rangle^2 = 12Ne^{-\epsilon/T}$, what does one learn about what is happening in the solution?

4. The polymer is then used in an experiment of atomic–force microscopy, fixing one end and applying to the other a constant force f. Estimate the average length $\langle L\rangle$ of the polymer.

Exercise 2

Consider n_A particles of type A and n_B particles of type B, with $n = n_A + n_B$. Each particle occupies a site of a lattice made of n sites, and double occupancy **is not** allowed.

1. Give the total number Γ of possible states of the system as a function of n and n_A.

2. By assuming $n, n_A, n_B \gg 1$, give the formula for the entropy, s, per lattice site of the system as a function of the fraction $\phi_A \equiv n_A/n$ of particles A.

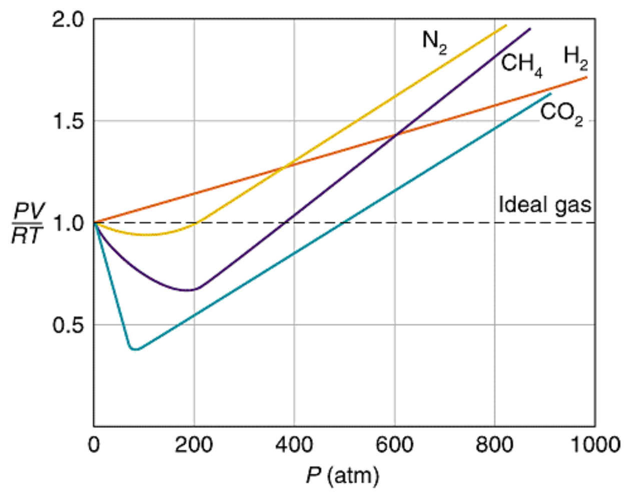
Assume now that site occupancy by a particle A is associated with an energy ϵ_A and by a particle B with an energy ϵ_B.

3. Compute the free energy, f, per lattice site of the system at temperature T.

4. Compute the expression ϕ_A for which the free energy attains its minimum value and briefly discuss it as a function of T.

Exercise 3

Real gases in nature deviate from the ideal-gas law. A manner in which this deviation can be quantified is by looking at the compressibility factor $\frac{PV}{RT}$. The Figure below shows this factor for a series of gases at a range of pressures for a fixed temperature.



1. Why does CO2 deviate the most from the ideal-gas law at low pressure?

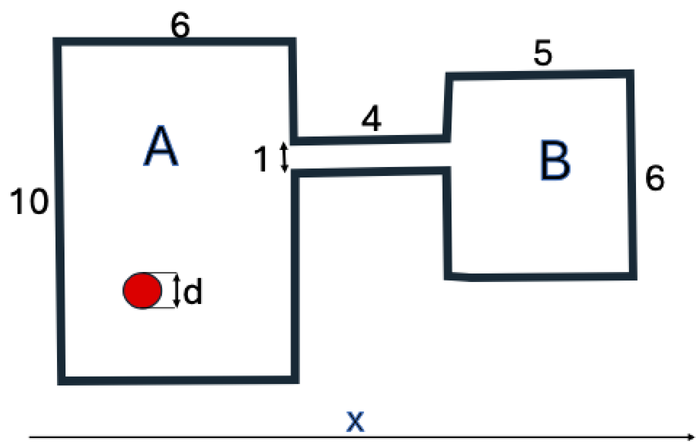
2. Why does the compressibility factor become positive at high pressure?

3. How would you correct the Pressure (P) and Volume (V) to account for the behaviour of real gases like CO2? Write explicitly the correction factors to *both* the Volume and Pressure.

4. Using Nitrogen gas an example, make a sketch of three curves (like the ones shown above), at 170K, 250K and 900K.

Exercise 4

A circular particle of diameter d is confined in the container depicted in figure and kept at a temperature T by a thermostat.



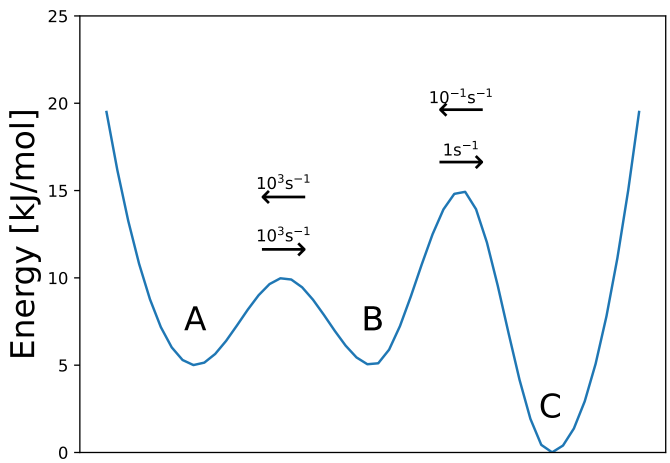
1. Compute the relative probability of observing the particle in chamber A and in chamber B.

2. Compute the free energy as a function of x. Plot the free energy $F(x)$ for $d = 0$

3. According to Arrenius law, the mean first passage time from A to B can be estimated as $\tau_{AB} = \tau_e \frac{P_A}{P_{barrier}}$, where P_A is the probability of observing the particle in chamber A and $P_{barrier}$ is the probability of observing it in the narrow passage between the two chambers. Assuming $\tau_e = 1$ s compute τ_{AB} as a function of d and of T. Discuss the dependence of τ_{AB} on the temperature. Plot τ_{AB} as a function of d.

Exercise 5

A system is diffusing on the energy profile represented in the figure. Transition rates are indicated in the figure.

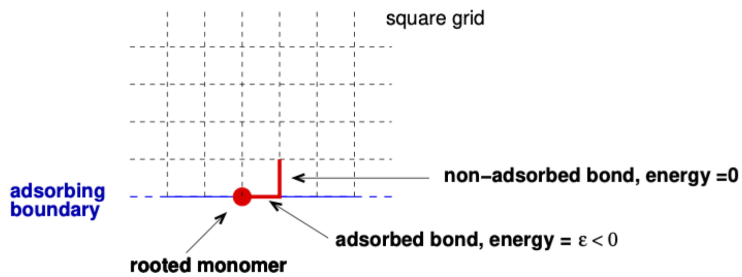


Answer the following questions:

1. At equilibrium, in which of the three states is the system most probably located?
2. Compute the stability of the three states at equilibrium.
3. Imagine that the system is initially located in A. Considering a timescale between 10^{-4}s and 10^{-2}s, plot the probability of finding the system in A, B, or C as a function of time.
4. Repeat the previous point considering a timescale between 10^{-1}s and 10s
5. For the two previous points, can you provide an analytical form for the probabilities as functions of time?
6. Considering the reported energy scale, can you guess which is the temperature of the system?
7. How much is the heat capacity of this system at low temperature?

Exercise 6

Consider a minimalistic model of lattice polymer, consisting of just $N = 2$ bonds, in the presence of an adsorbing boundary, as shown in the figure. The first monomer of the chain, which is self-avoiding, is rooted (pinned) on the boundary. The chain is in equilibrium at temperature T.



Address the following points:

1. Write down the partition function of the chain
2. Derive an expression for the average number of bonds, $\langle n_a \rangle$, that are adsorbed on the boundary and comment the result.
3. Derive an expression for the variance of the number of absorbed bonds and comment the result.
4. Consider now the $N \to \infty$ limit. Do you expect the chain to be always desorbed ($\lim_{N\to\infty} \langle n_a \rangle / N = 0$) in this case? Motivate your answer with qualitative and quantitative arguments.