

Ch/ChE 164 Winter 2024

Midterm

Due Date: Wednesday, February 7, 2024

Midterm Policy

- This is an open-book exam. You may look at your notes, your homework, the course notes, and the books listed on the course syllabus.
- You may not refer to homework or exams from previous years. You may not consult the internet outside of the course canvas page.
- You may take as long as you need before the due date to work on the exam.
- You may not consult with one another.
- Please write clearly and show all steps; points will be deducted if the midterm is unclear or illegible.
- Midterm must be turned in by the end of day on the due date. Late midterm will be penalized 10% per day unless prior arrangements have been made with the instructor.

Some identities that may or may not be useful (not necessarily exhaustive)...

$$(x + y)^N = \sum_{n=0}^N \binom{N}{n} x^n y^{N-n} \quad (1)$$

$$(1 + x)^N = \sum_{n=0}^N \binom{N}{n} x^n = \sum_{n=0}^N \binom{N}{n} x^n (1)^{N-n} \quad (2)$$

$$\frac{1}{1 - x} = \sum_{n=0}^{\infty} x^n \text{ for } |x| < 1 \quad (3)$$

$$\cosh(x) = \frac{e^x + e^{-x}}{2} = \frac{d}{dx} \sinh(x) \quad (4)$$

$$\sinh(x) = \frac{e^x - e^{-x}}{2} = \frac{d}{dx} \cosh(x) \quad (5)$$

$$\tanh(x) = \frac{\sinh(x)}{\cosh(x)} \quad (6)$$

- 1. Cross-linking polymer chain (30 pts)** Consider polymer chains, each with N monomers, all of which can reversibly associate with any other monomer. For simplicity, let us consider a single polymer chain at temperature T .

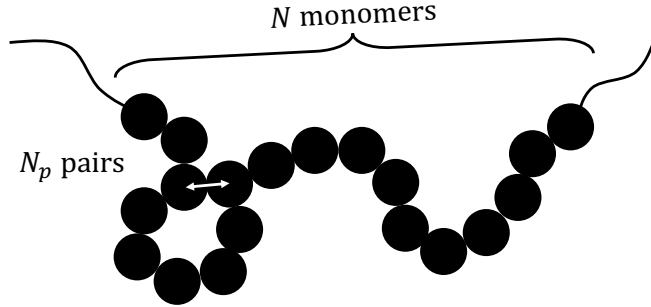


Figure 1: Visualisation of a polymer chain with N monomers forming a single, reversible pair.

- (a) (3 pts) How many ways can you select monomers from the chain to form N_p pairs?
- (b) (5 pts) From these monomers you've selected in **1a**, how many ways can you form N_p pairs (it may be easier to first consider the case where you can form 2 pairs from 4 monomers)?

Note: You may need to use $(N-1)!! = (N-1) \times (N-3) \times \dots$. This can be simplified using: $(N-1)!! = N! / [(N/2)! 2^{N/2}]$.

- (c) (6 pts) The product from **1a** and **1b** will give you the microcanonical partition function for a system with N_p pairs as:

$$\Omega(N, N_p) = \frac{N!}{(N - 2N_p)! N_p! 2^{N_p}} \quad (7)$$

If the energetic gain from forming a single pair is $-\epsilon$, write out the canonical partition function, $Q(N, T)$, for this system. You should end up with a sum over all possible values of N_p .

- (d) (10 pts) Find the most-probable term in this sum, and show that the corresponding value for the fraction of monomers associated ($p = 2N_p/N$) is given by:

$$p = 1 - \frac{\frac{\exp(-\beta\epsilon)}{N} - \sqrt{(2 + \frac{\exp(-\beta\epsilon)}{N})^2 - 4}}{2} \quad (8)$$

- (e) (6 pts) Let us now consider the limits of the fraction of monomers associated. Consider both the limit at high ($\beta \rightarrow 0$) and low ($\beta \rightarrow \infty$) temperatures. In terms of energetic interactions and conformational contributions, which effect dominates in either limit?

2. A diluted magnetic fluid (30 pts)

Consider a lattice with N lattice sites and n spins in an external magnetic field H that is pointing *up*. The lattice need not have every site filled with a spin.

- Spins can be either up or down, corresponding to $s_i = +1$ and $s_i = -1$. Spins aligned parallel to the field have an energy $-H$ whereas spins antiparallel have energy H .
- Vacant sites have no spin and thus no interaction with a magnetic field.

You can think of this as a crude model for a paramagnetic fluid that has some non-magnetic impurities. The lattice is connected to a reservoir at temperature T and chemical potential μ such that energy E and number of spins n are allowed to fluctuate. We can call this a **constrained grand canonical ensemble** because the particle number (n) can fluctuate, but cannot exceed N since the lattice has a fixed number of sites. *In this case N acts like V because $V = Nv_{\text{site}}$ where v_{site} is just the volume of a single lattice site.*

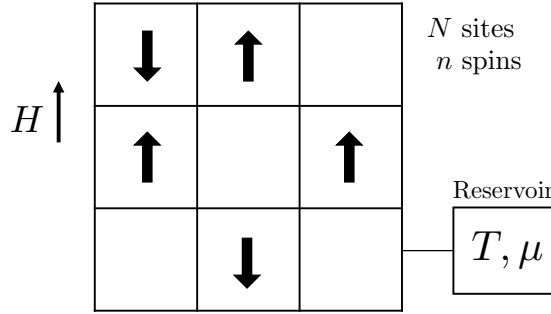


Figure 2: System schematic for the diluted paramagnetic fluid. The example here is showing the case for $N = 9$ and $n = 5$. Note that n fluctuates by exchanging with the reservoir.

- (a) (2 pts) What are the definitions of **microstate** and **macrostate** for this system?
- (b) (8 pts) Derive the closed-form grand canonical partition function $\Xi(N, T, \mu, H)$.

Start from either equality below

$$\Xi(N, T, \mu, H) = \sum_{\nu} e^{-\beta E_{\nu} + \beta \mu n_{\nu}} = \sum_n Q(N, T, n, H) e^{\beta \mu n} \quad (9)$$

and show that

$$\Xi(N, T, \mu, H) = \left[1 + 2e^{\beta \mu} \cosh(\beta H) \right]^N \quad (10)$$

There are multiple ways to do this!

- (c) (6 pts) Solve for the average fraction of occupied sites in the system $\langle x \rangle = \langle n \rangle / N$ using an appropriate derivative. What happens as $H \rightarrow \infty$? Explain the physical intuition of the limiting behavior.
- (d) (3 pts) In the reservoir, we have $H = 0$. If we also know that the fraction of sites occupied in the reservoir is x_R , then what is $e^{\beta\mu}$?
- (e) (4 pts) Calculate the average magnetisation $\langle M \rangle$.

Note the differential form of the grand free energy including the magnetisation

$$dW = -SdT - P v_{site} dN - nd\mu - MdH \quad (11)$$

- (f) (3 pts) Calculate the magnetic susceptibility, $\chi = (\partial \langle M \rangle / \partial H)_{T, N, \mu}$.
- (g) (4 pts) Relate the susceptibility χ to the fluctuations in magnetisation σ_M^2 . How does $\sigma_M / \langle M \rangle$ scale with N ? *This should require little additional work!*

3. Simple Elastic Molecule under Fixed Tension (40 pts)

A crude way to treat a rubber band is by treating it as a chain of linked segments that can take configurations of different lengths. In general we could also assume that the different configurations have different energies.

Assume that there are N total distinguishable segments which each have access to two different conformations: type **A** and type **B**. The types are distinguished by their length and their energy.

- Type **A** has length a and energy ϵ_a .
- Type **B** has length b and energy ϵ_b .

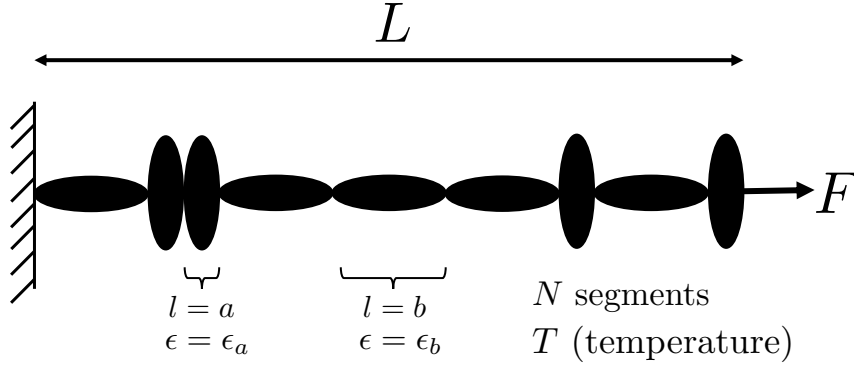


Figure 3: Schematic for the elastic molecule. Note that in this case L can fluctuate by changing segment conformations (**not** by changing N). The specific example shown is for $N = 9$ and $L = 4a + 5b$.

- (a) (8 pts) The molecule is placed in a bath at temperature T and extended with a fixed force F . Starting from the Euler equation for the relevant free energy at fixed (N, F, T) , use the variational method to derive the probability distribution $P_\nu(N, F, T)$ and show that the partition function $Z(N, F, T)$ in this ensemble is given by:

$$Z(N, F, T) = \sum_{\nu} e^{\beta F L_{\nu}} e^{-\beta E_{\nu}} \quad (12)$$

Note that the Euler equation and fundamental equation for the internal energy are, respectively:

$$E = TS + FL + \mu N \quad (13)$$

$$dE = TdS + FdL + \mu dN \quad (14)$$

- (b) (6 pts) Using the answer to part (a), show that the partition function in the (N, F, T) ensemble is given by

$$Z(N, F, T) = \left[e^{\beta F a} e^{-\beta \epsilon_a} + e^{\beta F b} e^{-\beta \epsilon_b} \right]^N \quad (15)$$

We will now look at a specific case, that yields some very interesting results. Let's take the simplest example, where $\epsilon_a = \epsilon_b = 0$ and $a = 0$. Thus, each segment is either vertical (and has no length) or is horizontal (and has length b). In this case, the partition function simplifies to,

$$Z(N, F, T) = \left[1 + e^{\beta F b} \right]^N \quad (16)$$

- (c) (4 pts) Calculate the extension-force equation of state, $\langle L \rangle = L(N, F, T)$.

$$\langle L \rangle = Nb \frac{e^{\beta F b}}{1 + e^{\beta F b}} \quad (17)$$

- (d) (4 pts) Find the equilibrium length (L_0) of the molecule at zero tension (i.e. at $F = 0$). Does this answer make sense? Why or why not?
- (e) (6 pts) Now we will derive Hooke's law and calculate the spring constant using statistical mechanics!
- i. Invert $L(N, F, T)$ to get the force-extension equation of state, $F(\langle L \rangle, N, T)$.
 - ii. Taylor expand $F(\langle L \rangle, N, T)$ out to first order around the equilibrium chain length from **3d**. Physically, when does this approximation apply?
 - iii. Extract the spring constant K_s by inspection.
- (f) (4 pts) Relate the fluctuations in length σ_L^2 at $F = 0$ to the spring constant, K_s . Explain why this relationship physically makes sense.
- (g) (8 pts) For this more simplified model of the chain where each segment is either vertical or horizontal, we can analyze the behavior using a fixed energy and length ensemble (i.e. the microcanonical ensemble). The partition function is given by $\Omega(N, L, E)$.
- i. Calculate the microcanonical partition function at length $L = nb$, where n is the number of horizontal segments.
 - ii. Show that your answer to **3d** maximizes the entropy.
 - iii. Verify that you obtain the same force-extension equation of state $F(N, L, T)$ in this ensemble.