

Ch/ChE 164 Winter 2024 Homework Problem Set #6

Due Date: Thursday, February 29, 2024 @ 11:59pm PT
Out of 100 Points

1

Project - Work on Question 1

1. Consider a liquid at temperature T in equilibrium with its vapor (at pressure p). Assume that the liquid-vapor interface is planar and that the vapor can be regarded as ideal.
 - (i) (20 points) Use the Maxwell-Boltzmann distribution to find the average number of vapor molecules that hit the interface per unit area per unit time.
 - (ii) (10 points) If a fraction ϕ of these molecules are bounced back, find the rate of evaporation of the liquid, i.e., the number of molecules that evaporate from the liquid per unit area per unit time.

2

2. (20 points) Derive the adsorption isotherm for a 2-component ideal gas containing species A and B . Assume that each adsorption site can only be singly occupied. The adsorption energy for species A is $-\varepsilon_A$ and that for species B is $-\varepsilon_B$. Express your result in terms of the partial pressures of each component.

3

3. For the noninteracting Ising model, the joint probability for the system factorizes into a product of the probability for each spin, i.e., $P(\{s\}) = \prod_i p_i(s_i)$.

3.1

(i) (5 points) Show that the Gibbs entropy is now

$$S = -k \sum_i \sum_{s_i} p_i(s_i) \ln p_i(s_i) \quad (1)$$

The expression for the Gibbs entropy is given by:

$$S = -k \sum_{[s]} P(\{s\}) \ln P(\{s\}) \quad (1)$$

where $[s]$ denotes the set of all possible spin configurations and $P(\{s\})$ is the probability of the system being in the configuration $\{s\}$. We insert the probability distribution given above into this expression:

$$S = -k \sum_{[s]} \prod_i p_i(s_i) \ln \prod_i p_i(s_i) \quad (2)$$

We can use the fact that the logarithm of a product is the sum of the logarithms of the factors:

$$S = -k \sum_{[s]} \sum_i \ln p_i(s_i) \prod_i p_i(s_i) \quad (3)$$

We can use the fact that the spins are not interacting to chance introduce a song over the individual spins at a given site s_i :

$$S = -k \sum_i \sum_{s_i} p_i(s_i) \ln p_i(s_i) \quad (4)$$

3.2

(ii) (5 points) Introducing the order parameter (average spin) $m_i = \langle s_i \rangle$, show that the variational free energy is

$$G = - \sum_i h_i m_i + kT \sum_i \left(\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right) \quad (2)$$

The free energy is given by:

$$G = E - TS \quad (5)$$

where E is the energy of the system and S is the entropy. We found the energy of the system in the lecture and it is given by:

$$\langle E \rangle = - \sum_i h_i \langle s_i \rangle = - \sum_i \sum_{s_i} h_i s_i p_i(s_i) \quad (6)$$

So using our previously derived expression for the entropy, we can plug in to the above equation for the free energy:

$$G = - \sum_i \sum_{s_i} h_i s_i p_i(s_i) - kT \sum_i \sum_{s_i} p_i(s_i) \ln p_i(s_i) \quad (7)$$

But we know that the sum of the probabilities that a given state has a spin pointing up or down has to be 1: $p_i(s_i = 1) + p_i(s_i = -1) = 1$. Also, from the definition of the magnetization we know that $m_i = \langle s_i \rangle = p_i(s_i = 1) - p_i(s_i = -1)$. So we can write the spin probability in terms of the magnetization as:

$$p_i(s_i = \pm 1) = \frac{1 \pm m_i}{2} \quad (8)$$

We can use this to get rid of the sum over the individual spins at a given site and rewrite this in terms of the magnetization:

$$G = - \sum_i h_i m_i - kT \sum_i \left(\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right) \quad (9)$$

3.3

(iii) (10 points) Show that minimization of this free energy yields the same equation of state as obtained in class by directly working with the partition function. Also show that the minimized free energy is the same as obtained in class using the partition function.

We want to minimize the previous expression for the free energy with respect to the magnetization at a given state:

$$\frac{\partial G}{\partial m_i} = 0 \quad (10)$$

Taking the first derivative of the above expression for the free energy. The first term will vanish unless the magnetization of the state we are taking the derivative with respect to is the same as the magnetization within the summation, so it simplifies to one turn of the sum:

$$\frac{\partial(-\sum_i h_i m_i)}{\partial m_i} = -h_i \quad (11)$$

For the second term the summation will vanish for the same reason as before, so we get for all of this:

$$\frac{\partial G}{\partial m_i} = -T \cdot k \cdot \left(-\frac{1}{2} \log \left(\frac{1}{2} - \frac{m_i}{2} \right) + \frac{1}{2} \log \left(\frac{m_i}{2} + \frac{1}{2} \right) \right) - h_i \quad (12)$$

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1 # Correct the free energy equation G by removing the
  incorrect sum usage
2 G = -hi * mi - k * T * ((1 + mi) / 2 * ln((1 + mi) / 2) + (1
  - mi) / 2 * ln((1 - mi) / 2))
3
4 # Compute the first derivative of G with respect to mi
  correctly
5 dG_dmi_correct = diff(G, mi)
6
7 dG_dmi_correct

```

Now, we said this equal to 0 and solve for m_i :

$$m_i = -\tanh \left(\frac{\log(\exp(2h_i))}{2Tk} \right) = \tanh(\beta h_i) \quad (13)$$

```

1 from sympy import solve, log
2
3 # Set the derivative equal to zero and solve for mi
4 solution = solve(dG_dmi_correct, mi)
5
6 solution

```

Now we want to plug this versal in to the expression for the free energy that we derived in the previous part, which is:

$$G = - \sum_i h_i m_i - kT \sum_i \left(\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right) \quad (14)$$

We plug in our expression for the magnetization:

$$G = - \sum_i h_i \tanh(\beta h_i) - kT \sum_i \left(\frac{1+\tanh(\beta h_i)}{2} \ln \frac{1+\tanh(\beta h_i)}{2} + \frac{1-\tanh(\beta h_i)}{2} \ln \frac{1-\tanh(\beta h_i)}{2} \right) \quad (15)$$

4

4. For the 1-dimensional Ising model with periodic boundary condition, the Hamiltonian is given by

$$H = -K (s_1 s_2 + s_2 s_3 + \dots + s_N s_1) - h \sum_{i=1}^N s_i \quad (3)$$

Use the transfer matrix method to obtain an exact solution in the limit of large N . In particular,

4.1

- (i) (10 points) Show that the partition function is given by

$$Z = \text{Tr}(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N \approx \lambda_+^N \quad (4)$$

with the transfer matrix

$$\mathbf{T} = \begin{pmatrix} e^{\beta K + \beta h} & e^{-\beta K} \\ e^{-\beta K} & e^{\beta K - \beta h} \end{pmatrix} \quad (5)$$

and λ_+ the larger of the two eigenvalues of the transfer matrix, λ_+ and λ_- . We started by diagnosing the transfer matrix, which gives the Iran values:

$$\lambda_+ = \frac{\sqrt{(e^{\beta(K-h)} + e^{\beta(K+h)})^2 - 8 \sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \quad (16)$$

and

$$\lambda_- = -\frac{\sqrt{(e^{\beta(K-h)} + e^{\beta(K+h)})^2 - 8 \sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \quad (17)$$

```

1 from sympy import Matrix, symbols, exp, simplify
2
3 # Define symbols
4 beta, K, h = symbols('beta K h')
5
6 # Define the transfer matrix T
7 T = Matrix([[exp(beta * K + beta * h), exp(-beta * K)],
8             [exp(-beta * K), exp(beta * K - beta * h)]])
9
10 # Diagonalize the transfer matrix T
11 eigenvals = T.eigenvals()
12 eigenvals_simplified = [simplify(val) for val in eigenvals.
13                           keys()]
14
15 # Since the user asked for the larger eigenvalue, let's
16   identify it
17 lambda_plus = max(eigenvals_simplified, key=lambda x: x.subs
18                   ({beta: 1, K: 1, h: 1}))
19 lambda_minus = min(eigenvals_simplified, key=lambda x: x.subs
20                    ({beta: 1, K: 1, h: 1}))
21
22 lambda_plus, lambda_minus

```

This will allow us to affectionately take the power of the trace with the metro since if it were not diagonal, this would be nonsensical. Now come in diagonal form this matrix is:

$$\mathbf{T} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \quad (18)$$

If we take the cancer matrix to the power of N we get:

$$\mathbf{T}^N = \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix} \quad (19)$$

So the trace of this matrix is:

$$\text{Tr}(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N \quad (20)$$

4.2

(ii) (10 points) Show that the eigenvalues are

$$\lambda_{\pm} = e^{\beta K} \cosh(\beta h) \pm \sqrt{e^{2\beta K} \sinh^2(\beta h) + e^{-2\beta K}} \quad (6)$$

We found the the again values from the symbol diagonalization of the transfer matrix:

$$\lambda_+ = \frac{\sqrt{(e^{\beta(K-h)} + e^{\beta(K+h)})^2 - 8 \sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \quad (21)$$

and

$$\lambda_- = -\frac{\sqrt{(e^{\beta(K-h)} + e^{\beta(K+h)})^2 - 8 \sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \quad (22)$$

For the term outside of the square root we can take out a common factor of $e^{\beta K}$ and use the identity $\cosh(\beta h) = \frac{e^{\beta h} + e^{-\beta h}}{2}$ to simplify the expression:

$$\lambda_{\pm} = e^{\beta K} \cosh(\beta h) \pm \frac{\sqrt{(e^{\beta(K-h)} + e^{\beta(K+h)})^2 - 8 \sinh(2K\beta)}}{2} \quad (23)$$

We see that the exponential term inside of the prentices can also be turned into a cosh term using the identity $\cosh(\beta h) = \frac{e^{\beta h} + e^{-\beta h}}{2}$:

$$\lambda_{\pm} = e^{\beta K} \cosh(\beta h) \pm \frac{\sqrt{(2e^{\beta K} \cosh(\beta h))^2 - 8 \sinh(2K\beta)}}{2} \quad (24)$$

4.3

(iii) (10 points) Examine and comment on the behavior of entropy and energy at $T = 0$ and $T = \infty$.

(iv) (Bonus 15 points) Show that the spin-spin correlation function at zero external field is given by

$$\langle s_i s_{i+r} \rangle = \frac{\lambda_+^{N-r} \lambda_-^r + \lambda_-^{N-r} \lambda_+^r}{\lambda_+^N + \lambda_-^N} \approx \left(\frac{\lambda_-}{\lambda_+} \right)^r \equiv e^{-r/\xi} \quad (7)$$

with the correlation length

$$\xi = \left[\ln \left(\frac{\lambda_+}{\lambda_-} \right) \right]^{-1} = -\frac{1}{\ln \tanh(\beta K)} \quad (8)$$

For Problem 4, you may consult any reference materials, including books and online resources. However, the work you write down must reflect your own understanding.