Ch/ChE 164 Winter 2024 Homework Problem Set #6

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

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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.

1.1

(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. The distributio is given by:

$$f(\mathbf{v})\,\mathrm{d}\mathbf{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m|\mathbf{v}|^2}{2kT}\right)\mathrm{d}\mathbf{v} \tag{1}$$

where m is the mass of the molecule, k is the Boltzmann constant, and T is the temperature. We know that $|\mathbf{v}|^2 = v_x^2 + v_y^2 + v_z^2$. We are interested in the slugs to through and interface, so we want to consider the expectation value of the speed in the z direction.

$$\langle v_z\rangle = \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} \exp\left(-\frac{mv_x^2}{2kT}\right)\mathrm{d}v_x \int_{-\infty}^{\infty} \exp\left(-\frac{mv_y^2}{2kT}\right)\mathrm{d}v_y \int_{-\infty}^{\infty} v_z \exp\left(-\frac{mv_z^2}{2kT}\right)\mathrm{d}v_z \tag{2}$$

The first two integrals are just cations that each evaluate to $\sqrt{2\pi kT/m}$, so we are left with:

$$\langle v_z \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{-\infty}^{\infty} v_z \exp\left(-\frac{mv_z^2}{2kT}\right) \mathrm{d}v_z \tag{3}$$

But we only care about the velocity in the positive direction, so this becomes:

$$\langle v_{z+} \rangle = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{0}^{\infty} v_z \exp\left(-\frac{mv_z^2}{2kT}\right) \mathrm{d}v_z \tag{4}$$

$$\langle v_{z+} \rangle = \frac{\sqrt{2kT}}{2\sqrt{\pi m}} \tag{5}$$

```
from sympy import *

# Define symbols for this \langle v_{z+} \rangle = \left(\frac{m}{2\pi k T}\right)^{1/2} \int_{0}^{\infty} v_z \exp\left(-\frac{m v_z^2}{2 k T}\right) \dd{v_z}
m, T, k = symbols('m T k', real=True, positive=True)
v_z = symbols('v_z', real=True)

# Define the integrand
integrand = v_z * exp(-m * v_z**2 / (2 * k * T))

# Compute the integral
integral = integrate(integrand, (v_z, 0, oo))

# Simplify the result
integral = simplify(integral)

# multiply by the prefactor
integral = sqrt(m / (2 * pi * k * T)) * integral

# simplify the result
integral = simplify(integral)

# Print the result
print(latex(integral))
```

The total flux j is given by:

$$j = \rho \langle v_{z+} \rangle \tag{6}$$

From the ideal gas law, we get that $\rho = \frac{p}{kT}$, so the flux is:

$$j = \frac{p}{kT} \frac{\sqrt{2kT}}{2\sqrt{\pi m}} \tag{7}$$

1.2

(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.
For computing the rat of evaporation, we want to instead consider the compliment of the fraction of molecules bouncing back, or $1-\phi$. So the rate of evaporation is:

$$j_{\text{evap}} = j \cdot (1-\phi) = \frac{p}{kT}\frac{\sqrt{2kT}}{2\sqrt{\pi m}} \cdot (1-\phi) \tag{8}$$

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.

2.1

The grand canonical partition function is given by

$$\Xi\left(N, T, \mu_A, \mu_B\right) = \sum_{N_A=0}^{N} \sum_{N_B=0}^{N-N_A} \left(\begin{array}{c} N \\ N_A \end{array}\right) \left(\begin{array}{c} N-N_A \\ N_B \end{array}\right) e^{\beta N_A(\mu_A+\epsilon_A)} e^{\beta N_B(\mu_B+\epsilon_B)} \tag{9}$$

We will attempt to explain this form. The first submission is over the first species and it runs from 0 to the total particle number. The second submission is similar and it runs from 0 to the number of particles left after the first selection. The first binomial coefficient represents the number of ways to choose N_A particles from the total number of particles. The second binomial coefficient represents the number of ways to choose N_B particles from the remaining number of particles after the first selection. The first exponential term represents the energy and chemical potential contribution from the first species and the second exponential term represents the energy and chemical potential contribution from the second species. We can use the multinomial theorem to simplify this expression:

$$\Xi(N,T,\mu_A,\mu_B) = (1 + e^{\beta(\mu_A+\epsilon_A)} + e^{\beta(\mu_B+\epsilon_B)})^N \tag{10}$$

The fraction of sites occupied by species A is $\Theta_A = \frac{\langle N_A\rangle}{N}$ and the fraction of sites occupied by species B is $\Theta_B = \frac{\langle N_B\rangle}{N}$. We want to find $\langle N_A\rangle$ and $\langle N_B\rangle$. We know that the grand potential is given by:

$$\Omega = -kT\ln\Xi \tag{11}$$

and then also the differential of the grand potential is given by:

$$\mathrm{d}\Omega = -S\,\mathrm{d}T - P\,\mathrm{d}V - \sum_i \mu_i\,\mathrm{d}N_i = -S\,\mathrm{d}T - P\,\mathrm{d}V - N_A\,\mathrm{d}\mu_A - N_B\,\mathrm{d}\mu_B \tag{12}$$

So the expectation value of the particle number of the first species is given by:

$$\langle N_A\rangle = -\left(\frac{\partial\Omega}{\partial\mu_A}\right)_{T,V,\mu_B} = \left(\frac{\partial\ln\Xi}{\partial\beta\mu_A}\right)_{T,V,\mu_B} \tag{13}$$

So, using this algorithm, we can get Θ_A and Θ_B.

$$\Theta_A = \frac{\exp\left(\frac{\epsilon_A+\mu_A}{kT}\right)}{\exp\left(\frac{\epsilon_A+\mu_A}{kT}\right) + \exp\left(\frac{\epsilon_B+\mu_B}{kT}\right) + 1} \tag{14}$$

$$\Theta_B = \frac{\exp\left(\frac{\epsilon_B+\mu_B}{kT}\right)}{\exp\left(\frac{\epsilon_A+\mu_A}{kT}\right) + \exp\left(\frac{\epsilon_B+\mu_B}{kT}\right) + 1} \tag{15}$$

```
from sympy import symbols, exp, diff, solve, ln, simplify

# Define symbols
N, T, beta, mu_A, mu_B, epsilon_A, epsilon_B = symbols('N
    T beta mu_A mu_B epsilon_A epsilon_B')
N_A, N_B = symbols('N_A N_B')
k = symbols('k')

# Define the grand canonical partition function
  simplified expression
Xi = (1 + exp(beta*(mu_A + epsilon_A)) + exp(beta*(mu_B +
    epsilon_B)))**N
```

```

# Calculate the grand potential Omega
Omega = -k*T*ln(Xi)

# Calculate the expectation value of N_A and N_B
dOmega_dmuA = diff(Omega, mu_A)
dOmega_dmuB = diff(Omega, mu_B)

# Solve for <N_A> and <N_B>
N_A_avg = -dOmega_dmuA
N_B_avg = -dOmega_dmuB

# Calculate the fraction of sites occupied by species A and B
Theta_A = N_A_avg / N
Theta_B = N_B_avg / N

simplify(N_A_avg), simplify(N_B_avg), simplify(Theta_A), simplify(Theta_B)
```

We have $\theta_A\left(T, \epsilon_A, \epsilon_B, \mu_A, \mu_B\right)$ and we want to go to $\theta_A\left(T, \epsilon_A, \epsilon_B, P_A, P_B\right)$. We can use the equality of the chemical potentials in adsorption:

$$\beta\mu_A^{\text{ads}} = \beta\mu_A^{\text{free}} = \rho_A \Lambda_A^3 \tag{16}$$

And from that ideal gas law, we know that $\rho_A = \frac{P_A}{kT}$, so we can write:

$$\beta\mu_A^{\text{ads}} = \frac{P_A \Lambda_A^3}{kT} \tag{17}$$

and for the second species:

$$\beta\mu_B^{\text{ads}} = \frac{P_B \Lambda_B^3}{kT} \tag{18}$$

Substituting these into the expression for Θ_A and $\Theta_B$and simplifying::

$$\Theta_A = \frac{\Lambda_A^3 P_A \exp\left(\frac{\epsilon_A}{Tk}\right)}{\Lambda_A^3 P_A \exp\left(\frac{\epsilon_A}{Tk}\right) + \Lambda_B^3 P_B \exp\left(\frac{\epsilon_B}{Tk}\right) + Tk} \tag{19}$$

$$\Theta_B = \frac{\Lambda_B^3 P_B \exp\left(\frac{\epsilon_B}{Tk}\right)}{\Lambda_A^3 P_A \exp\left(\frac{\epsilon_A}{Tk}\right) + \Lambda_B^3 P_B \exp\left(\frac{\epsilon_B}{Tk}\right) + Tk} \tag{20}$$

```
# Define new symbols for partial pressures P_A and P_B, and thermal de Broglie wavelengths Lambda_A and Lambda_B
P_A, P_B, Lambda_A, Lambda_B = symbols('P_A P_B Lambda_A Lambda_B')

# Replace beta * mu_A and beta * mu_B in the expressions for Theta_A and Theta_B
Theta_A_expr = exp((epsilon_A + k*T*ln(P_A * Lambda_A**3 / (k*T)))/(k*T)) / \
                (exp((epsilon_A + k*T*ln(P_A * Lambda_A**3 / (k*T)))/(k*T)) +
                 exp((epsilon_B + k*T*ln(P_B * Lambda_B**3 / (k*T)))/(k*T)) + 1)

Theta_B_expr = exp((epsilon_B + k*T*ln(P_B * Lambda_B**3 / (k*T)))/(k*T)) / \
                (exp((epsilon_A + k*T*ln(P_A * Lambda_A**3 / (k*T)))/(k*T)) +
                 exp((epsilon_B + k*T*ln(P_B * Lambda_B**3 / (k*T)))/(k*T)) + 1)

simplify(Theta_A_expr), simplify(Theta_B_expr)
```

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

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

The expression for the Gibbs entropy is given by:

$$S = -k \sum_{[s]} P(\{s\}) \ln P(\{s\}) \tag{21}$$

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:

$$S = -k \sum_{[s]} \prod_i p_i\left(s_i\right) \ln \prod_i p_i\left(s_i\right) \tag{22}$$

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

$$S = -k \sum_{[s]} \sum_i \ln p_i\left(s_i\right) \prod_i p_i\left(s_i\right) \tag{23}$$

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:

$$S = -k \sum_i \sum_{s_i} p_i\left(s_i\right) \ln p_i\left(s_i\right) \tag{24}$$

3.2

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

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

The free energy is given by:

$$G = E - TS \tag{25}$$

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:

$$\langle E \rangle = -\sum_i h_i \langle s_i \rangle = -\sum_i \sum_{s_i} h_i s_i p_i\left(s_i\right) \tag{26}$$

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

$$G = -\sum_i \sum_{s_i} h_i s_i p_i\left(s_i\right) + kT \sum_i \sum_{s_i} p_i\left(s_i\right) \ln p_i\left(s_i\right) \tag{27}$$

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

$$p_i\left(s_i=\pm 1\right)=\frac{1\pm m_i}{2} \tag{28}$$

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

$$G=-\sum_i h_i m_i+kT\sum_i\left(\frac{1+m_i}{2}\ln\frac{1+m_i}{2}+\frac{1-m_i}{2}\ln\frac{1-m_i}{2}\right) \tag{29}$$

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:

$$\frac{\partial G}{\partial m_i}=0 \tag{30}$$

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 two is the same as the magnetization within the summation, so it simplifies to one turn of the sum:

$$\frac{\partial(-\sum_i h_i m_i)}{\partial m_i}=-h_i \tag{31}$$

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

$$\frac{\partial G}{\partial m_i}=-T\cdot k\cdot\left(-\frac{1}{2}\log\left(\frac{1}{2}-\frac{m_i}{2}\right)+\frac{1}{2}\log\left(\frac{m_i}{2}+\frac{1}{2}\right)\right)-h_i \tag{32}$$

```
# Correct the free energy equation G by removing the
    incorrect sum usage
G = -hi * mi - k * T * ((1 + mi) / 2 * ln((1 + mi) / 2) + (1
    - mi) / 2 * ln((1 - mi) / 2))

# Compute the first derivative of G with respect to mi
    correctly
dG_dmi_correct = diff(G, mi)

dG_dmi_correct
```

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

$$m_i = -\tanh\left(\frac{\log\left(\exp\left(2h_i\right)\right)}{2Tk}\right) = \tanh\left(\beta h_i\right) \tag{33}$$

```
from sympy import solve, log

# Set the derivative equal to zero and solve for mi
solution = solve(dG_dmi_correct, mi)

solution
```

Now, that we have found this equation of state, we want to plug it back into our expression for the variational free energy:

$$G = -\sum_i h_i \tanh\left(\beta h_i\right) + kT \sum_i \left(\frac{1+\tanh\left(\beta h_i\right)}{2} \ln \frac{1+\tanh\left(\beta h_i\right)}{2} + \frac{1-\tanh\left(\beta h_i\right)}{2} \ln \frac{1-\tanh\left(\beta h\right.}{2} \tag{34}$$

4

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

$$H = -K\left(s_1 s_2 + s_2 s_3 + \cdots + s_N s_1\right) - h \sum_{i=1}^{N} s_i \tag{3}$$

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

$$Z = \mathrm{Tr}\left(\mathbf{T}^N\right) = \lambda_+^N + \lambda_-^N \approx \lambda_+^N \tag{4}$$

with the transfer matrix

$$\mathbf{T} = \begin{pmatrix} \mathrm{e}^{\beta K+\beta h} & \mathrm{e}^{-\beta K} \\ \mathrm{e}^{-\beta K} & \mathrm{e}^{\beta K-\beta h} \end{pmatrix} \tag{5}$$

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

$$\lambda_+ = \frac{\sqrt{\left(e^{\beta(K-h)} + e^{\beta(K+h)}\right)^2 - 8\sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \tag{35}$$

and

$$\lambda_- = -\frac{\sqrt{\left(e^{\beta(K-h)} + e^{\beta(K+h)}\right)^2 - 8\sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \tag{36}$$

```python
from sympy import Matrix, symbols, exp, simplify

# Define symbols
beta, K, h = symbols('beta K h')

# Define the transfer matrix T
T = Matrix([[exp(beta * K + beta * h), exp(-beta * K)],
            [exp(-beta * K), exp(beta * K - beta * h)]])

# Diagonalize the transfer matrix T
eigenvals = T.eigenvals()
eigenvals_simplified = [simplify(val) for val in eigenvals.
    keys()]

# Since the user asked for the larger eigenvalue, let's
    identify it
lambda_plus = max(eigenvals_simplified, key=lambda x: x.subs
    ({beta: 1, K: 1, h: 1}))
lambda_minus = min(eigenvals_simplified, key=lambda x: x.subs
    ({beta: 1, K: 1, h: 1}))

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:

$$\mathbf{T} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \tag{37}$$

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

$$\mathbf{T}^N = \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix} \tag{38}$$

So the trace of this matrix is:

$$\mathrm{Tr}\left(\mathbf{T}^N\right) = \lambda_+^N + \lambda_-^N \tag{39}$$

Because λ_+ is even slightly larger than λ_-, in the thermo dynamic limit with a large N, we can approximate:

$$\mathrm{Tr}\left(\mathbf{T}^N\right) \approx \lambda_+^N \tag{40}$$

4.2

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

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

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

$$\lambda_+ = \frac{\sqrt{\left(e^{\beta(K-h)} + e^{\beta(K+h)}\right)^2 - 8\sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \tag{41}$$

and

$$\lambda_- = -\frac{\sqrt{\left(e^{\beta(K-h)} + e^{\beta(K+h)}\right)^2 - 8\sinh(2K\beta)}}{2} + \frac{e^{\beta(K-h)}}{2} + \frac{e^{\beta(K+h)}}{2} \tag{42}$$

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:

$$\lambda_\pm = \mathrm{e}^{\beta K} \cosh(\beta h) \pm \frac{\sqrt{\left(e^{\beta(K-h)} + e^{\beta(K+h)}\right)^2 - 8\sinh(2K\beta)}}{2} \tag{43}$$

4.3

(iii) (10 points) Examine and comment on the behavior of entropy and energy at $T = 0$ and $T = \infty$. Since we know the partition function, the expression for the energy is:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{44}$$

We start by considering $\ln Z$:

$$\ln Z = N \ln \lambda_+ \tag{45}$$

taking the derivative with respect to β, we get:

$$\langle E \rangle = -N \left(\frac{K e^{2\beta K} + h \sinh(\beta h)}{\sqrt{e^{4\beta K} \sinh^2(\beta h) + 1}} + K \right) \tag{46}$$

In the limit of $T = 0$, $\beta \to \infty$, the energy will be:

$$\langle E \rangle = -N \left(\frac{K e^{2\beta K}}{e^{2\beta K} \sinh(\beta h)} + K \right) = -N \left(\frac{K}{\sinh(\beta h)} + K \right) = -NK \tag{47}$$

In the limit of $T = \infty$, $\beta \to 0$, the energy will be:

$$\langle E \rangle = -N \left(\frac{1}{1} + K \right) = -N(1 + K) \tag{48}$$

```python
from sympy import symbols, exp, cosh, sinh, sqrt, diff, ln

# Define symbols
beta, K, h, N = symbols('beta K h N', real=True)

# Define lambda_+ based on the given expression
lambda_plus = exp(beta * K) * cosh(beta * h) + sqrt(exp(2 *
    beta * K) * sinh(beta * h)**2 + exp(-2 * beta * K))

# Compute the derivative of ln(lambda_+) with respect to beta
d_ln_lambda_plus_dbeta = diff(ln(lambda_plus), beta)

# Energy expression
E = -N * d_ln_lambda_plus_dbeta

E.simplify()
```

We know that:

$$S = k(\ln Z + \beta E) \tag{49}$$

Substituting in the expression for the partition function:

$$S = k\left(N \ln \lambda_+ + \beta E\right) \tag{50}$$

Now, we substitute for the energy and λ_+:

$$S = k\left(N \ln \lambda_+ + \beta E\right) = k\left(N \ln \lambda_+ - \beta N\left(\frac{Ke^{2\beta K} + h\sinh(\beta h)}{\sqrt{e^{4\beta K}\sinh^2(\beta h) + 1}} + K\right)\right) \tag{51}$$

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

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

with the correlation length

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

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.