

Chem 322: Physical Chemistry II

Spring 2025 Exam 1
Professor Yuting Chen

Name: _____

This is an open note exam. You may use your prepared two-page cheat sheet and calculator, but no other external resources. No other electronics may be in your possession. The Hamilton College Honor Code applies to this exam.

By my signature below, I affirm on my honor the work represented in this exam is solely my own, and that I did not give or receive assistance on this exam. Violating the Honor Code will result in automatic failure of the course.

Signature: _____

Instructions

- Do not turn this page until instructed to do so.
- Ensure you have all pages of the exam. The exam consists of one cover page and 9 pages of questions.
- Write your answers in the space indicated by the test. Anything written on the back will not be graded. If you need additional space, ask for scratch paper.
- Write legibly. Answers that cannot be read may not receive credit.
- Please show all of your work. Even if the final answer is correct, you will not receive credit if the corresponding work is missing or incomplete.
- Grading is based on the consistency of your work. If you make an error in one step, you may still receive credit for later steps if your other steps are consistent, so it is in your best interest to attempt all parts of a problem.
- Include units for all of your answers. Report answers with a reasonable number of significant figures unless otherwise specified.

1. Partition Function

The partition function is a key quantity in statistical mechanics that describes a systems thermodynamic behavior. Concisely (2-3 sentences max) answer the following questions about its significance.

- (a) (4 points) What role does the partition function play in normalizing probabilities?

The probability of finding in a state i with energy E_i is $e^{-\beta E_i}$. We are summing over these probabilities and want the probability to normalize to 1, so the normalizing factor for all of these probabilities is $\frac{1}{Q} = \frac{1}{\sum e^{-\beta E_i}}$

- (b) (4 points) How is the partition function related to the number of microstates and their occupation probabilities?

The partition function is defined as $Q = e^{-\beta E_0} + e^{-\beta E_1} \dots$. Each individual term represents the occupation probability of a given state, and the partition function arises from summing over the total number of microstates.

- (c) (4 points) How does the partition function connect microscopic molecular behavior to macroscopic system properties?

The molecular partition function sums over the microscopic molecular contributions, and is related to the system partition function by $Q = q^N$ or $Q = q^N/N!$. We can take derivatives of Q to arrive at macroscopic properties like heat capacity, pressure, and energy

- (d) (2 points) What are the units of the partition function?

Unitless

2. Law of Dulong and Petit

The Law of Dulong and Petit is an empirical rule in thermodynamics that states the heat capacity of crystalline solids is given by: $\overline{C}_v = 3R$. In this problem we will be deriving this law.

- (a) (3 points) The molecular partition function to use in this *classical derivation* is given an integral rather than a typical summation. Why is this the case?

$$q = \int e^{-\beta\varepsilon} d\varepsilon$$

Classical energies are continuous, so we use an integral for a continuous distribution instead of a summation for a discrete one.

- (b) (5 points) Because this is a *classical derivation*, rather than using our quantum harmonic oscillator model that has energy $E_n = h\nu(n + \frac{1}{2})$, we need to use a classical harmonic oscillator with a spring constant k and mass m moving in one dimension. That energy is given by $\varepsilon = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$. Using this definition of energy, integrate to derive an expression for q . Because ε depends on both x and v , we need to perform a double integral:

$$q = \int dv \int dx e^{-\beta\varepsilon(v,x)}$$

The following integral should be helpful:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

Separate the integral:

$$q = \left(\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}mv^2} dv \right) \left(\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}kx^2} dx \right)$$

Using the provided gaussian integral:

$$q = \left(\sqrt{\frac{2\pi}{\beta m}} \right) \left(\sqrt{\frac{2\pi}{\beta k}} \right) = \frac{2\pi}{\beta} \sqrt{\frac{1}{mk}}$$

- (c) (3 points) Now that you have your molecular partition function q , calculate the system partition function Q . Remember this system is a 3 dimensional crystal with N *indistinguishable* atoms occupying the crystal lattice.

The 3D partition function is $q_{3D} = q^3$. Then to account for N atoms we raise to the N power and divide by $N!$.

$$Q = \frac{(q_{3D})^N}{N!} = \frac{q^{3N}}{N!} = \frac{1}{N!} \left(\frac{2\pi}{\beta} \sqrt{\frac{1}{mk}} \right)^{3N}$$

- (d) (6 points) Finally, finish the derivation by calculating $\langle E \rangle$ and \overline{C}_V . If everything is done correctly, you should get $\overline{C}_V = 3R$

$$\langle E \rangle = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} = \frac{\partial}{\partial \beta} (3N \ln \beta + \text{constant terms}) = \boxed{3Nk_B T}$$

$$\overline{C}_V = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \frac{\partial}{\partial T} (3Nk_B T) = 3Nk_B = \boxed{3R}$$

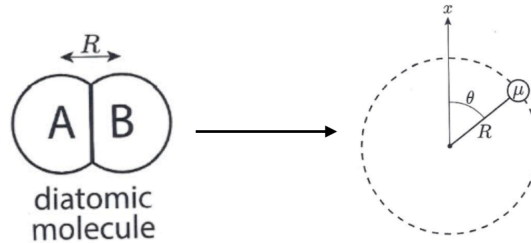
- (e) (6 points) While we are on the topic of heat capacities, use the equipartition theorem to determine the molar heat capacities for CH_3OH , XeF_2 , and Cl_2 at high temperatures.

Molecule	Trans.	Rot.	Vibr.	$C_V (R)$
CH_3OH (nonlinear)	3	3	$3(6) - 6 = 12$	$\frac{3}{2} + \frac{3}{2} + 12 = \boxed{15R}$
XeF_2 (linear)	3	2	$3(3) - 5 = 4$	$\frac{3}{2} + \frac{2}{2} + 4 = \boxed{\frac{13}{2}R}$
Cl_2 (linear)	3	2	$3(2) - 5 = 1$	$\frac{3}{2} + \frac{2}{2} + 1 = \boxed{\frac{7}{2}R}$

3. Rotational Partition Function of a Confined Molecule

This problem involves developing a model to describe a small molecule bound to a surface, such as a protein attached to a biological membrane.

Consider a diatomic molecule confined to a two-dimensional plane, where the internuclear distance is R . We focus only on rotational degrees of freedom, ignoring translational and vibrational motion. The rotation of this diatomic molecule in the plane is mathematically equivalent to the motion of an effective particle with mass μ on a ring of radius R .



This particle-in-a-ring model yields the quantized rotational energy levels with quantum number n :

$$E_n = cn^2, \quad n = \dots, -2, -1, 0, 1, 2, \dots$$

where $c = \frac{\hbar^2}{2\mu R^2}$, \hbar is Planck's constant, and $\hbar = \frac{h}{2\pi}$.

- (a) (4 points) Write the rotational partition function, $q_{\text{rot}}(\beta)$, as a summation. A closed-form expression is not required.

$$q_{\text{rot}}(\beta) = \sum_{n=-\infty}^{\infty} e^{-\beta E_n} = \sum_{n=-\infty}^{\infty} e^{-\beta cn^2}$$

Alternatively, you could account for the degeneracy by recognizing that n^2 is symmetric about $n = 0$ and write:

$$q_{\text{rot}}(\beta) = 1 + 2 \sum_{n=1}^{\infty} e^{-\beta cn^2}$$

- (b) (5 points) Since evaluating the summation exactly is difficult, approximate $q_{\text{rot}}(\beta)$ by treating n as a continuous variable. This allows us to replace the summation with an integral. Use this method to evaluate $q_{\text{rot}}^{\text{approx}}(\beta)$.

The following integral should be helpful:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$q_{\text{rot}}^{\text{approx}}(\beta) \approx \int_{-\infty}^{\infty} e^{-\beta c n^2} dn$$

Recognizing $\alpha = \beta c$, we get:

$$q_{\text{rot}}^{\text{approx}}(\beta) = \sqrt{\frac{\pi}{\beta c}}$$

Or using the definition of c :

$$q_{\text{rot}}^{\text{approx}}(\beta) = \sqrt{\frac{2\pi\mu R^2}{\beta\hbar^2}}$$

- (c) (3 points) Using the equipartition theorem, determine the rotational contribution to the average energy, $\langle E_{\text{rot}} \rangle$. You may assume that we are at high temperature.

Each degree of freedom contributes $\frac{1}{2}k_B T$. Normally for linear diatomics we have 2 degrees of freedom, but because the molecule is constrained, we only have 1 degree of freedom. Thus $\langle E_{\text{rot}} \rangle = \frac{1}{2}k_B T$

- (d) (10 points) Using the approximate partition function $q_{\text{rot}}^{\text{approx}}(\beta)$, calculate the rotational contribution to the average energy, $\langle E_{\text{rot}} \rangle$.

Compare this result to the one obtained using the equipartition theorem. Do the two results agree? Explain why or why not.

Starting from our partition function:

$$q_{\text{rot}}^{\text{approx}}(\beta) = \sqrt{\frac{\pi}{\beta c}}$$

We take the natural log and evaluate the partial derivative to get average energy:

$$\ln q_{\text{rot}}^{\text{approx}}(\beta) = \ln \left(\sqrt{\frac{\pi}{\beta c}} \right)$$

$$\langle E_{\text{rot}} \rangle = -\frac{\partial \ln q_{\text{rot}}^{\text{approx}}(\beta)}{\partial \beta} = -\frac{\partial}{\partial \beta} \left(-\frac{1}{2} \ln \beta - \text{constant terms} \right)$$

Then we replace $\beta = \frac{1}{k_B T}$:

$$\langle E_{\text{rot}} \rangle = \frac{1}{2\beta} = \frac{1}{2} k_B T$$

These results should match, as they are two different ways to model the same system: rotations in a diatomic molecule

4. Two Level System

Consider a system consisting of two *distinguishable* particles. Each particle can occupy one of two possible energy levels: $\varepsilon_0 = 0$ or $\varepsilon_1 = \varepsilon$. For this parts a-c, any final expression for Q should be fully expanded, do not leave it as a summation.

- (a) (4 points) Determine the total number of microstates in this system, and write the partition function Q for the whole system.

There are 4 distinct microstates: $(0, 0), (0, \varepsilon), (\varepsilon, 0), (\varepsilon, \varepsilon)$

$$Q = \sum_i \Omega e^{-\beta E_i} = 1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

- (b) (4 points) Suppose the particles are now *indistinguishable*. How many microstates are in the new system, and what is the new partition function?

There are 3 distinct microstates: $(0, 0), (0, \varepsilon), (\varepsilon, \varepsilon)$

$$Q = \sum_i e^{-\beta E_i} = 1 + e^{-\beta\varepsilon} + e^{-\beta 2\varepsilon}$$

- (c) (4 points) Suppose the particles are now *indistinguishable electrons*. How many microstates are in the new system, and what is the new partition function?

There is 1 microstates due to the Pauli Exclusion principle: $(0, \varepsilon)$

$$Q = e^{-\beta\varepsilon}$$

Consider the same two-level system, now consisting of N *distinguishable* particles instead of 2, but the same energy levels are allowed. The average energy per particle is given by $\langle E \rangle / N$.

- (d) (4 points) Without performing any calculations, explain what value you expect $\langle E \rangle / N$ to be at the high temperature ($T \rightarrow \infty$) and the low temperature ($T \rightarrow 0$) limit.

At high temperature we expect equal occupancy of all states, so both state $\varepsilon_0 = 0$ or $\varepsilon_1 = \varepsilon$ will be equally occupied by $N/2$ particles, resulting in average energy per particle $\langle E \rangle / N = \frac{1}{N} \left(\frac{N}{2}(0) + \frac{N}{2}(\varepsilon) \right) = \frac{\varepsilon}{2}$

At low temperature we expect only the ground state to be occupied with average energy per particle $\langle E \rangle / N = \frac{1}{N}(0) = 0$

- (e) (10 points) Determine the maximum value of $\langle E \rangle / N$ and the temperature corresponding to it. Start from this result we derived for a homework assignment:

$$\langle E \rangle = \frac{N\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

Recall our conversion, and we need to take a partial wrt T to maximize:

$$\frac{\partial}{\partial T} = -\frac{1}{k_B T^2} \cdot \frac{\partial}{\partial \beta}$$

We have to take the partial wrt β using product/quotient rule:

$$\begin{aligned} \frac{\partial}{\partial \beta} \left(\frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}} \right) &= \frac{(1 + e^{-\beta\varepsilon})(-\varepsilon^2 e^{-\beta\varepsilon}) - (\varepsilon e^{-\beta\varepsilon})(-\varepsilon e^{-\beta\varepsilon})}{(1 + e^{-\beta\varepsilon})^2} \\ &= \frac{-\varepsilon^2 e^{-\beta\varepsilon} - \varepsilon^2 e^{-2\beta\varepsilon} + \varepsilon^2 e^{-2\beta\varepsilon}}{(1 + e^{-\beta\varepsilon})^2} \\ &= \frac{-\varepsilon^2 e^{-\beta\varepsilon}}{(1 + e^{-\beta\varepsilon})^2}. \end{aligned}$$

Putting it all together:

$$\frac{d}{dT} \left(\frac{\langle E \rangle}{N} \right) = \frac{\varepsilon^2 e^{-\beta\varepsilon}}{k_B T^2 (1 + e^{-\beta\varepsilon})^2} = 0$$

$\frac{1}{(1 + e^{-\beta\varepsilon})^2}$ is always nonzero, so we have to either have $\frac{1}{k_B T^2} = 0$ or $e^{-\beta\varepsilon} = 0$. The first one yields $T = \infty$, the second one yields $\beta = \infty \rightarrow T = 0$. We know these values from part d! $T = \infty$ is the T_{max} , corresponding to $\frac{\langle E \rangle}{N} = \frac{\varepsilon e^0}{1 + e^0} = \frac{\varepsilon \cdot 1}{1 + 1} = \frac{\varepsilon}{2}$

5. Challenge Problem: Average Pressure

(a) (15 points) Prove that:

$$\left(\frac{\partial \langle P \rangle}{\partial \beta}\right)_{N,V} = \langle E \rangle \langle P \rangle - \langle EP \rangle$$

First let us substitute in our definitions $P_i = -\left(\frac{\partial E_i}{\partial V}\right)_N$ and $p_i = \frac{e^{-\beta E_j}}{Q}$:

$$\left(\frac{\partial \langle P \rangle}{\partial \beta}\right)_{N,V} = \frac{\partial}{\partial \beta} \left(\sum_i p_i P_i \right) = \frac{\partial}{\partial \beta} \left(-\frac{1}{Q} \sum_i \left(\frac{\partial E_i}{\partial V} \right) e^{-\beta E_i} \right)$$

This is a product rule since $Q(N, V, \beta)$ and the exponential depend on β but $\frac{\partial E_i}{\partial V}$ does not:

$$\left(\frac{\partial \langle P \rangle}{\partial \beta}\right)_{N,V} = \left(\frac{\partial}{\partial \beta} \frac{1}{Q}\right) \left(-\sum_i \left(\frac{\partial E_i}{\partial v}\right) e^{-\beta E_j} \right) + \frac{1}{Q} \left(+\sum_i \left(\frac{\partial E_i}{\partial v}\right) E_i e^{-\beta E_i} \right)$$

We now evaluate the first term using the chain rule, recalling $Q = \sum_i e^{-\beta E_i}$:

$$\frac{\partial}{\partial \beta} \frac{1}{Q} = -\frac{1}{Q^2} \frac{\partial Q}{\partial \beta} = +\frac{1}{Q^2} \sum_j E_j e^{-\beta E_j}$$

Substituting this into the first term and replacing $P_i = -\left(\frac{\partial E_i}{\partial V}\right)_N$ we now get:

$$\left(\frac{\partial \langle P \rangle}{\partial \beta}\right)_{N,V} = \underbrace{\frac{\sum_i E_i e^{-\beta E_i}}{Q}}_{\langle E \rangle} \underbrace{\left(\frac{\sum_i P_j e^{-\beta E_j}}{Q}\right)}_{\langle P \rangle} - \underbrace{\frac{\sum_i P_i E_j e^{-\beta E_i}}{Q}}_{\langle EP \rangle}$$

Therefore we have shown:

$$\left(\frac{\partial \langle P \rangle}{\partial \beta}\right)_{N,V} = \langle E \rangle \langle P \rangle - \langle EP \rangle$$