Chem 322: Physical Chemistry II

Spring 2026 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 the page until instructed. You have 4 hours for the exam.
- Ensure you have all pages of the exam. The exam consists of one cover page and 6 pages of questions.
- Write your answers in the spaces indicated. Anything written on the backs of pages will not be graded. If you need more space, ask for scratch paper.
- Write legibly and show all of your work clearly and logically. Even if the final answer is correct, you may not receive credit if your work is incomplete, indecipherable, or unable to be followed.
- 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. **Zeeman Effect**

A single particle is placed in a constant magnetic field B, and has energy

$$E_m = m\mu B$$

Where μ is the constant chemical potential, and $m = -1, 0, 1$ is the magnetic moment.

(a) (4 points) Write the canonical partition function in terms of $B, \mu,$ and β.

$$Q = \sum_i e^{-\beta E_i} = \sum_{i=-1}^{1} e^{-\beta E_i} = e^{\beta\mu B} + 1 + e^{-\beta\mu B}$$

(b) (8 points) Compute the average energy by taking partial derivatives. You do not need to significantly simplify your result because we will do that in the next part.

We use the chain rule version $\langle E\rangle = -\frac{1}{Q}\frac{\partial Q}{\partial \beta}$:
Take the partial wrt to β:

$$\frac{\partial Q}{\partial \beta} = \frac{\partial}{\partial \beta}(e^{\beta\mu B} + 1 + e^{-\beta\mu B}) = \mu B\, e^{\beta\mu B} - \mu B\, e^{-\beta\mu B}$$

Therefore:

$$\langle E\rangle = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{\mu B\, e^{\beta\mu B} - \mu B\, e^{-\beta\mu B}}{e^{\beta\mu B} + 1 + e^{-\beta\mu B}} = \frac{-\mu B\, e^{\beta\mu B} + \mu B\, e^{-\beta\mu B}}{e^{\beta\mu B} + 1 + e^{-\beta\mu B}}$$

(c) (6 points) Use a first order Taylor expansion, $e^x \approx 1 + x$, to get the high-temperature limit of the average energy in terms of $B, \mu,$ and β.

Using the Taylor expansion:

$$e^{\beta\mu B} = 1 + \beta\mu B \qquad e^{-\beta\mu B} = 1 - \beta\mu B$$

We can simplify the numerator and denominators:

$$-\mu B(1 + \beta\mu B) + \mu B(1 - \beta\mu B) = -2(\mu B)^2\beta$$

$$(1 + \beta\mu B) + 1 + (1 - \beta\mu B) = 3$$

Thus:

$$\langle E \rangle = -\frac{2(\mu B)^2\beta}{3}$$

(d) (8 points) Evaluate the heat capacity in the high-temperature limit.

Use the definition:

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial \langle E \rangle}{\partial \beta}$$

Differentiate with respect to β:

$$\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{2(\mu B)^2\beta}{3}\right) = -\frac{2(\mu B)^2}{3}$$

Therefore:

$$C_V = -\frac{1}{k_B T^2}\left(-\frac{2(\mu B)^2}{3}\right) = \frac{2(\mu B)^2}{3k_B T^2}$$

$$\boxed{C_V = \frac{2(\mu B)^2}{3k_B T^2}}$$

2. **Counting Microstates**

Consider a system consisting of 5 *indistinguishable* particles and 10 energy levels, $\varepsilon_n = n, n = 0, 1, 2 \cdots 9$.

(a) (4 points) If each level can hold any number of particle, how many microstates are there?

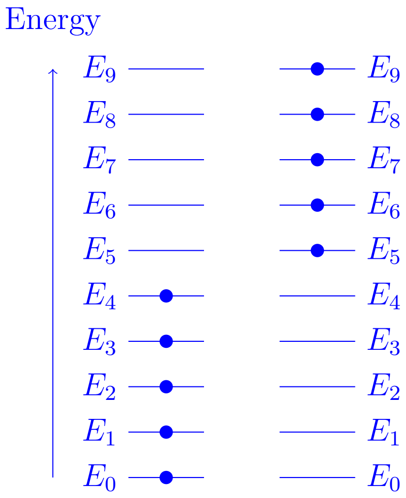
Stars and bars, 5 particles, 10 levels means 9 bars and 14 "things"

$$\binom{14}{9} = \frac{14!}{9! \cdot 5!} = 2002$$

(b) (4 points) If each level can hold at most one particle, how many microstates are there?

$$\binom{10}{5} = \frac{10!}{5! \cdot 5!} = 252$$

(c) (8 points) For the system decribed in (b), how many distinct exponential terms would appear in Q after accounting for degeneracy? Briefly (2–3 sentences) justify your answer. For example, $Q = e^{-\beta 0} + 2e^{-\beta E} + 4e^{-\beta 2E}$ would have 3 terms.
Hint: Do not try to enumerate. I intentionally made the answer to (b) high enough so that you cannot enumerate all microstates in the given time frame.



The lowest energy microstate has total energy

$$E = 0 + 1 + 2 + 3 + 4 = 10$$

The highest energy microstate has total energy

$$E = 5 + 6 + 7 + 8 + 9 = 35$$

Each energy level between these values can be accessed by moving particles between levels, so the range of values is $10 - 35$ which corresponds to $35 - 10 + 1 = \boxed{26 \text{ terms}}$

3. **Dieterici's Equation of State**

In classical thermodynamics, we've started to discuss equation of states like the Ideal Gas Law, van der Waal. Dieterici is another equation of state with partition function:

$$Q = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}(V - Nb)^N e^{\beta a N/V}$$

Where a is a correction for intermolecular forces and and b is correction factors for V.

(a) (4 points) Do you think Dieterici's Equation of State assumes distinguishable or indistinguishable particles? How can you tell?

Q has a factor of $1/N!$, so the particles are indistinguishable as the $1/N!$ corrects for overcounting microstates due to permuting particles.

(b) (10 points) Derive an expression for the average internal energy. Express your final answer in terms of T, not β.

The average internal energy is

$$U = -\frac{\partial \ln Q}{\partial \beta}$$
$$\ln Q = -\ln N! + \frac{3N}{2}\ln(2\pi m k_B T/h^2) + N\ln(V - Nb) + \beta a N/V$$

Split the derivative into two terms:

$$U = -\frac{\partial}{\partial \beta}\left[\frac{3N}{2}\ln(2\pi m k_B T/h^2)\right] - \frac{\partial}{\partial \beta}\left[\beta a N/V\right]$$

For the first term, convert to derivative with respect to T using $\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T}$:

$$\begin{aligned} U &= -\left(-k_B T^2 \frac{\partial}{\partial T}\right)\left[\frac{3N}{2}\ln(2\pi m k_B T/h^2)\right] - \frac{\partial}{\partial \beta}\left[\beta a N/V\right] \\ &= k_B T^2 \frac{\partial}{\partial T}\left[\frac{3N}{2}\ln T\right] - \frac{aN}{V} \\ &= k_B T^2 \cdot \frac{3N}{2}\cdot\frac{1}{T} - \frac{aN}{V} \\ &= \frac{3}{2}N k_B T - \frac{aN}{V} \end{aligned}$$

(c) (8 points) Derive an expression for the molar heat capacity. Connect your result to the equipartition theorem by determining what type of molecular motion is being modeled. You can consider both your answer to (c) and the form of the partition function.

$$\begin{aligned} C_V &= \frac{\partial}{\partial T}\left(\frac{3}{2}Nk_BT - \frac{aN}{V}\right) \\ &= \frac{3}{2}Nk_B = \frac{3}{2}nR \\ \overline{C_V} &= \frac{C_V}{n} = \frac{3}{2}R \end{aligned}$$

This matches the equipartition result for translational movement, each DOF is $\frac{1}{2}R$, so $\frac{3}{2}R$ for translational movement. Also agrees with the partition function as the $\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}$ closely resembles the translational partition function.

(d) (10 points) Derive an expression for the average pressure. Express your final answer in terms of T, not β.

$$Q = \frac{1}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}(V - Nb)^N e^{\beta aN/V}$$

The average pressure is

$$\begin{aligned} P &= k_BT\frac{\partial \ln Q}{\partial V} \\ \ln Q &= -\ln N! + \frac{3N}{2}\ln(2\pi mk_BT/h^2) + N\ln(V - Nb) + \frac{\beta aN}{V} \end{aligned}$$

Take the derivative with respect to V:

$$\begin{aligned} \frac{\partial \ln Q}{\partial V} &= \frac{\partial}{\partial V}\left[N\ln(V - Nb) + \frac{\beta aN}{V}\right] \\ &= \frac{N}{V - Nb} - \frac{\beta aN^2}{V^2} \end{aligned}$$

Multiply by k_BT to get the pressure:

$$\begin{aligned} P &= k_BT\left(\frac{N}{V - Nb} - \frac{\beta aN}{V^2}\right) \\ &= \frac{Nk_BT}{V - Nb} - \frac{aN}{V^2} \end{aligned}$$

4. **Molecular Partition Functions**

A student measures a molecule to have the following characteristic temperatures:
$\Theta_{rot} = 42$ K, $\Theta_{vib} = 67$ K.

(a) (8 points) Based on these numbers, determine the temperature range for which the molecule has greater than 50% probability of occupying an excited rotational state while simultaneously having less than 50% probability of occupying an excited vibrational state.

$$P_{\text{rot,excited}} = 1 - \frac{\Theta_{\text{rot}}}{T} \qquad P_{\text{vib,excited}} = e^{-\Theta_{\text{vib}}/T}$$

$$1 - \frac{\Theta_{\text{rot}}}{T} > 0.5 \implies \frac{\Theta_{\text{rot}}}{T} < 0.5 \implies T > 2\Theta_{\text{rot}} = 2(42) = 84\text{ K}$$

$$e^{-\Theta_{\text{vib}}/T} < 0.5 \implies \frac{\Theta_{\text{vib}}}{T} > -\ln 0.5 = 0.693 \implies T < \frac{\Theta_{\text{vib}}}{0.693} \approx \frac{67}{0.693} \approx 96.7\text{ K}$$

$$84\text{ K} < T < 96.7\text{ K}$$

(b) (4 points) Based on your knowledge of typical molecular rotational and vibrational energies, do the student's measured values seem reasonable? Explain your reasoning in 2–3 sentences.

No. Vibrational energy level spacings are significantly larger than rotational, seeing typical values $\Theta_{\text{vib}} \approx 1000K$, whereas $\Theta_{\text{rot}} < 10K$, so at least 2 orders of magnitude apart. Values of 42 K and 67 K are too close in magnitude and therefore not realistic.

5. **Equipartition**

Determine the molar heat capacities of the following molecules in the high temperature limit.

(a) (4 points) CH_3CN

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} + \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{rotational}} + \underbrace{12(R)}_{\text{vibrational}} = 3R + 12R = \boxed{15R}$$

(b) (4 points) Xe

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} = \boxed{\tfrac{3}{2}R}$$

(c) (4 points) $BeCl_2$

$$\overline{C_V} = \underbrace{3\left(\tfrac{1}{2}R\right)}_{\text{translational}} + \underbrace{2\left(\tfrac{1}{2}R\right)}_{\text{rotational}} + \underbrace{4(R)}_{\text{vibrational}} = \tfrac{5}{2}R + 4R = \boxed{\tfrac{13}{2}R}$$

(d) (2 points) At lower temperatures, which DOF does not contribute to the heat capacity?

Vibrational