EXAMINATION PAPER

Examination Session:	Year:	Exam Code:
May/June	2025	MATH42320-WE01

Title:

Statistical Mechanics V

Time:	3 hours	
Additional Material provided:		
Materials Permitted:		
Calculators Permitted:	No	Models Permitted: Use of electronic calculators is forbidden.

Instructions to Candidates:	Answer all questions. Section A is worth 40% and Section B is worth 60%. Within each section, all questions carry equal marks. Write your answer in the white-covered answer booklet with barcodes. Begin your answer to each question on a new page.

Revision:	

SECTION A

Q1 The van der Waals equation of state is a modification of the ideal gas equation of state. It reads

$$\left(p + \frac{N^2}{V^2} a\right)(V - Nb) = N k_B T \ , \tag{1}$$

where a and b are two positive parameters, and N is the number of gas molecules, which is held fixed in this question. The physical region is $V > Nb$. The internal energy of the van der Waals gas is

$$E = \alpha N k_B T - \frac{N^2 a}{V} \ , \tag{2}$$

where α is a positive constant.

Consider a Carnot engine for the van der Waals gas, which consists of the following four processes in order:

(i) Isothermal expansion from pressure p_A, volume V_A to pressure p_B, volume V_B at constant temperature T_H.

(ii) Adiabatic expansion from pressure p_B, volume V_B to pressure p_C, volume V_C.

(iii) Isothermal compression from pressure p_C, volume V_C to pressure p_D, volume V_D at constant temperature T_C.

(iv) Adiabatic compression from p_D, volume V_D to pressure p_A, volume V_A.

For this cycle, the 1st law takes the form $dE = TdS - pdV$.

(a) Compute the change in energy ΔE, the work W, and the heat Q_H during isothermal expansion (step (i)).

(b) Compute the change in entropy during isothermal compression. Is it positive or negative? Does this violate the 2nd law of thermodynamics?

(c) In problems class, we showed that the quantity

$$(V - Nb)T^{\alpha} \tag{3}$$

is constant during adiabatic compression or expansion of the van der Waals gas. Use this fact to derive the relation

$$\frac{(V_D - Nb)}{(V_C - Nb)} = \frac{(V_A - Nb)}{(V_B - Nb)} \,. \tag{4}$$

Q2 The Hamiltonian for a charged particle of mass m in three dimensions is given by:

$$\mathcal{H}(q_i, p_i) = \sum_{i=1}^{3} \frac{p_i^2}{2m} + \psi(q_j)\,, \tag{5}$$

where $i, j = 1, 2, 3$, and $\psi(q_j)$ is, in general, a function of all three position coordinates q_j.

Recall that the Poisson bracket is defined as $\{A, B\} = \sum_i (\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i})$, and Liouville's equation is given by $\frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\} = 0$.

(a) Write down Hamilton's equations for this system.

(b) Suppose next that

$$\psi(q_j) = \alpha q_1^2\,, \tag{6}$$

where α is a positive constant. Compute the Poisson brackets $\{\mathcal{H}, p_1^2\}$, $\{\mathcal{H}, p_2\}$, $\{\mathcal{H}, q_2\}$.

(c) We now study probability distributions $\rho(q, p; t)$ that evolve according to Hamiltonian evolution with Hamiltonian (5) with ψ given by (6). Which of the following probability distributions are solutions to Liouville's equation? Briefly explain your reasoning:

(i) $\rho_1(q_i, p_i) = \mathcal{N}_1 \exp(-\mathcal{H})$

(ii) $\rho_2(q_i, p_i) = \mathcal{N}_2 \exp(-\mathcal{H} + \alpha q_2)$

(iii) $\rho_3(q_i, p_i) = \mathcal{N}_3 \exp(-\mathcal{H} + \frac{p_2^2}{2m})$

(d) Suppose once again that ψ is given by (6), and consider an ensemble with $\rho(q, p, t)$ that obeys Liouville's equation and has the initial value $\rho(t = 0) = \mathcal{N} \exp(-\mathcal{H} + \alpha q_3)$. Let $\langle x \rangle$ denote the ensemble average of x. What is $\frac{d}{dt}\langle p_2 \rangle$? Justify your answer.

Q3 (a) Define the canonical ensemble, by specifying which quantities are kept fixed and writing down the appropriate probability distributions $p(|n\rangle)$.

(b) Show that this form of $p(|n\rangle)$ is the probability distribution that maximises the Gibbs entropy under the constraint that the average energy and the total probability are fixed. [Hint: use Lagrange multipliers to fix the constraints.]

(c) The method in part (b) used average energy in place of the thermodynamic quantity that is actually being kept fixed in the canonical ensemble. Explain using the scaling properties of the variance σ_E and the average energy $\langle E \rangle$ with particle number N why this is a reasonable assumption.

Q4 A hydrogen atom in equilibrium with radiation at temperature T has a single electron that can be in the ground state energy level which is a two-fold spin degenerate orbital with energy ε_0, or it can be in the first excited energy level which is a six-fold degenerate orbital with energy ε_1. For the purposes of this problem assume that the atom does not have any other excited states.

(a) What is the probability that the electron has energy ε_0 and what is the probability it has energy ε_1?

(b) If the temperature is such that $k_B T = \varepsilon_1 - \varepsilon_0$, determine which of the two orbital levels is occupied more.

(c) Derive an expression for the mean energy of the atom at temperature T and obtain the limiting value of this mean energy as $T \to \infty$.

SECTION B

Q5 In this problem we will consider the following Hamiltonian for a particle living in one dimension:

$$H(q,p)=\frac{p^2}{2m}+\alpha^2q^2+\beta q\,. \tag{7}$$

Here, α, β, and m are positive constants.

(a) In the microcanonical ensemble, compute the "area" of accessible states $\mathcal{N}(E)$ in the full phase space $\mathcal{P}$, defined as

$$\mathcal{N}(E)=\int_{\mathcal{P}}d\mu\delta(H(q,p)-E)\,. \tag{8}$$

It may help to suitably rescale and shift the integration variables to simplify the calculation of the integral.

(b) There is a critical energy E_c such that $\mathcal{N}(E)$ vanishes for $E<E_c$. Find E_c.

(c) Compute in the microcanonical ensemble the entropy $S(E)=k_B\log\Omega(E)$, where $\Omega(E)=\frac{\mathcal{N}}{\mathcal{N}_0}$, where we take $\mathcal{N}_0=\frac{h}{E}$, with h a constant.

(d) Does this system satisfy the third law of thermodynamics? Justify your answer.

(e) Compute the unconditional probability distribution $\rho_{\text{unc}}(p)$ of p in the microcanonical ensemble. You do not need to normalize it correctly: in this problem we are only asking for the p dependence.

Q6 Consider a particle moving in one dimension undergoing a random walk. At each time step, the particle takes a step s, whose size is drawn from a normalised probability distribution with probability density $w(s)$ given by:

$$w(s)=\mathcal{M}\exp\left(-\frac{|s|}{a}\right)\,, \tag{9}$$

with $a>0$.

(a) Calculate the constant $\mathcal{M}$ in terms of the width a, assuming that $w(s)$ is a properly normalized probability distribution function (PDF).

(b) What are the mean $\langle s\rangle$ and the variance $\langle s^2\rangle_c$ associated with the PDF $w(s)$?

(c) Calculate the characteristic function $\tilde{w}(k)$ associated with the PDF $w(s)$.

(d) Write down the joint PDF $p(s_1,s_2)$ for the variables s_1 and s_2, where s_i is the ith step of the particle. After $N=2$ steps, calculate the mean $\langle X\rangle$ and the variance $\langle X^2\rangle_c$ associated with the total displacement $X=s_1+s_2$.

(e) What is the probability that $(s_2-a)>s_1>0$?

Q7 A quantum string effectively consists of an infinite number of harmonic oscillators with natural frequencies given by $\omega_\ell = \ell\omega$ with $\ell \in \mathbb{N}$, where ω is the lowest vibrational frequency of the string. Thus if we subtract the zero-point energy, the Hamiltonian of such a system takes the form

$$H(\{N_\ell\}) \;=\; \sum_{\ell=1}^{\infty} \hbar\ell\omega N_\ell$$

where $N_\ell \in \mathbb{Z}^+$ (which includes 0) is the occupation number of the ℓ'th harmonic oscillator.

(a) By summing over all possible occupation numbers (assuming that they are not restricted) derive the grand canonical partition function $\mathcal{Z}$ for this system.

(b) Hence derive the grand canonical potential Φ (as a sum over ℓ).

(c) Assume that at large temperatures we may use the approximations that $\beta\hbar\omega \ll 1$ and that the fugacity $z = e^{\beta\mu} \approx 1$. Show that under these approximations the sum becomes an integral which evaluates to

$$\Phi \;\approx\; -\frac{\pi^2}{6\hbar\omega\beta^2}\ .$$

[Hint: you may use the expansion $\log(1-y) = -\sum_{m=1}^{\infty} \frac{y^m}{m}$ and the sum $\sum_{m=1}^{\infty} m^{-2} = \frac{\pi^2}{6}$, and swap infinite sums without justification.]

Q8 Imagine a pipe of cross-sectional area A going from the surface of the Earth right through the centre to the other side. The pipe is filled with a monatomic, non-relativistic gas and sealed at both ends. The gravitational field inside the Earth is proportional to the distance z from its centre, such that the potential energy experienced by a gas particle inside the pipe is

$$V(z) \;=\; mg\frac{z^2}{2a}$$

where a is the radius of the Earth.

(a) Assuming that the temperature is constant throughout the pipe, compute the probability distribution function $p(z)$ for the distance of a particle from the centre.

(b) Assuming that the gas particles are indistinguishable, calculate the canonical partition function Z in terms of temperature T, area A and radius a.

(c) Hence show that at high temperature, $k_BT \gg mga$, the pressure exerted by the gas on the ends of the pipe at the surface obeys the ideal gas law.

$\Big[$Hint: You may use the error function given by $\displaystyle\int_{-a}^{a} e^{-cz^2}dz = \frac{\sqrt{\pi}\,\mathrm{erf}\left(a\sqrt{c}\right)}{\sqrt{c}}$,
and the approximation that when $ca^2 \ll 1$ we have $\displaystyle\int_{-a}^{a} e^{-cz^2}dz \approx 2a\ .\Big]$