EXAMINATION PAPER

Examination Session: May	**Year:** 2017	**Exam Code:** MATH4231-WE01

Title: Statistical Mechanics IV

Time Allowed:	3 hours	
Additional Material provided:	None	
Materials Permitted:	None	
Calculators Permitted:	No	Models Permitted: Use of electronic calculators is forbidden.
Visiting Students may use dictionaries: No		

Instructions to Candidates:	Credit will be given for: the best **TWO** answers from Section A, the best **THREE** answers from Section B, **AND** the answer to the question in Section C. Questions in Section B and C carry **TWICE** as many marks as those in Section A.

Revision:	

ED01/2017

Useful formulae:

- The volume of a ball $B^n = \{(x_1, x_2, \dots, x_n) \mid x_1^2 + x_2^2 + \cdots + x_n^2 \leq R^2\}$ and the surface area of a sphere $S^{n-1} = \{(x_1, x_2, \dots, x_n) \mid x_1^2 + x_2^2 + \cdots + x_n^2 = R^2\}$ of radius R in n dimensions are:

$$\mathrm{Vol}(B^n) = \frac{\pi^{n/2}}{\Gamma(n/2+1)}\, R^n \ , \qquad \mathrm{Area}(S^{n-1}) = \frac{2\,\pi^{n/2}}{\Gamma(n/2)}\, R^{n-1} \ .$$

- The one-dimensional Gaussian integral:

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}} \ .$$

- Stirling's formula:

$$\log n! \approx n \log n - n \ .$$

- Gamma function – definition and properties:

$$\Gamma(x) = \int_0^\infty e^{-z}\, z^{x-1}\, dz \qquad \mathrm{Re}(x) > 0 \ ,$$

$$\begin{aligned} \Gamma(x+1) &= x\,\Gamma(x) \\ \Gamma\left(1/2\right) &= \sqrt{\pi} \\ \Gamma(n+1) &= n! \qquad (n \in \mathbb{N}) \ . \end{aligned}$$

- Dirac delta function:

$$\delta(x) = \int_{-\infty}^{\infty} \frac{dk}{2\pi}\, e^{i\,k\,x}$$

- Partial sum of a geometric series:

$$\sum_{n=0}^{p} x^n = 1 + x + x^2 + \cdots + x^p = \frac{1 - x^{p+1}}{1 - x} \ .$$

SECTION A

1. Consider a system whose entropy fundamental relation is

$$S(E,V,N) = c\,\left(E\,V^3\,N\right)^{1/5}\ ,$$

for some positive constant c.

(a) Show that the entropy is extensive.

(b) Derive the energy fundamental relation

$$E = E(S,V,N)$$

and compute the intensive quantities in terms of the extensive quantities:

$$T = T(S,V,N)\ ,\quad p = p(S,V,N)\ ,\quad \mu = \mu(S,V,N)\ .$$

(c) Find the behaviour of the entropy of the system as $T \to 0$, keeping V and N fixed. Does the system satisfy the Third Law of Thermodynamics?

2. An ideal monatomic gas consists of N free particles moving in a 3-dimensional box of volume V at temperature T.

(a) Write down the equation of state of the ideal gas and the total internal energy of the ideal gas according to the equipartition theorem. Justify the latter formula.

(b) Calculate the heat capacities C_V and C_p at constant volume or pressure, keeping N fixed.

(c) Define a reversible adiabat. Show that the equation for a reversible adiabat in the (V,p)-plane is $pV^\gamma = \text{const}$, where $\gamma = C_p/C_V$.

3. (a) Starting from the internal energy $E(S,V,N)$, define the following thermodynamic potentials by appropriate Legendre transforms:

   i. Helmholtz free energy $F(T,V,N)$;
   ii. Gibbs free energy $G(T,p,N)$;
   iii. Enthalpy $H(S,p,N)$.

(b) Using the form of dE given by the First Law of Thermodynamics, write the differential expressions for each of the above thermodynamics potentials.

(c) Use (b) at fixed number of particles N to derive the Maxwell relation

$$\left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p\ .$$

4. Consider a quantum system with discrete states $|n\rangle$, and neglect any possible dependence on the volume in the following discussion.

   Define the following statistical ensembles, by specifying which quantities are kept fixed and writing down the appropriate discrete probability distributions $p(n)$:

   (a) Microcanonical ensemble.

   (b) Canonical ensemble.

   (c) Grand canonical ensemble.

5. Consider an isolated system of N non-interacting distinguishable particles, each of which can sit in either the ground state, with energy $E_0 = 0$, or the excited state, with energy $E_1 = \epsilon$.

   (a) Which quantities specify the macrostate of the system in the microcanonical ensemble?

   (b) How are the microstates that correspond to a given macrostate characterised? Count the number Ω of such microstates.

   (c) Compute the entropy of the system in the thermodynamic limit where the internal energy E and the total number of particles N are large, using Boltzmann's formula and Stirling's approximation.

6. Consider a quantum system of non-interacting fermions that can occupy discrete states $|r\rangle$.

   (a) Write down the Fermi-Dirac distribution for the average number of fermions $\langle n_r \rangle$ that occupy state $|r\rangle$. Which values can $\langle n_r \rangle$ take and why? How does the Fermi-Dirac distribution differ from the Bose-Einstein distribution?

   (b) Derive the extreme low temperature limit $T \to 0$ of the Fermi-Dirac distibution. What is its physical interpretation? Give a physical definition of the Fermi energy E_F and provide a mathematical formula for it.

SECTION B

7. Consider N classical harmonic oscillators in 1 dimension, each with Hamiltonian

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 \ ,$$

which are far enough from each other and are therefore distinguishable. Calculate the thermodynamical properties of the system in the canonical ensemble as follows:

(a) Write down and compute the partition function for a single oscillator $Z_1(\beta)$, and from this deduce the N-oscillator partition function $Z_N(\beta)$. Is there a Gibbs factor $\frac{1}{N!}$?

(b) Compute the free energy $F(T,N)$ of the system from the partition function.

(c) Compute the entropy $S(T,N)$ of the system from the partition function.

(d) Compute the internal energy $\langle E\rangle$ of the system from the partition function. Does it obey the equipartition theorem? Justify your answer.

(e) Using the previous formulae, check that the relations $F = \langle E\rangle - TS$ and $S = -\frac{\partial F}{\partial T}\big|_{V,N}$ hold.

(f) What is the pressure p of the system and why?

(g) Compute the chemical potential μ of the system.

8. A 1-dimensional random walk describes a particle which moves randomly in a lattice in 1-dimension with spacing a. The lattice is labelled by a coordinate $x = ma$, where m is an integer. The particle starts from $x = 0$. At every iteration it can move either one step to the right ($m \to m+1$), with probability r, or one step to the left ($m \to m-1$), with probability $s = 1 - r$.

(a) What is the probability $p_N(n_R)$ that in N steps the particle moves n_R steps to the right and $n_L = N - n_R$ steps to the left? Relate the random variable x, that is the net displacement of the particle after N steps, to the random variable n_R.

(b) Use the result of (a) to calculate the mean value $\langle x\rangle$ of the net displacement of the particle after N steps.

(c) Calculate the variance σ_x^2 of the net displacement after N steps.

(d) Calculate $\tilde{p}_N(k) = \langle \exp(-ikx)\rangle$, the generating function of moments of the net displacement, and the generating function of cumulants $\ln \tilde{p}_N(k)$.

(e) How do the cumulants depend on the number of steps N? Use this result to deduce the limiting probability distribution $p_{N=\infty}(y)$ for the variable

$$y = \frac{x - \langle x\rangle}{\sqrt{N}}$$

when $N \to \infty$.

9. A diatomic gas consists of molecules made of two atoms. In addition to the three translational degrees of freedom of the centre of mass, each molecule can rotate rigidly about the two axes perpendicular to the axis of symmetry, and vibrate along the axis of symmetry.

   (a) Compute the rotational contribution $Z^{(c)}_{\text{rot}}$ to the classical partition function of one gas molecule, using the rotational Hamiltonian

   $$H_{\text{rot}}(\theta, \phi, p_\theta, p_\phi) = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta} \ .$$

   Here (θ, ϕ) are the standard polar and azimuthal angle that parametrise a 2-sphere in 3 dimensions, p_θ and p_ϕ are the conjugate momenta, which can take any real values, and I is the moment of inertia.

   (b) Quantum-mechanically, the rotational Hamiltonian has energy levels

   $$E_j = \frac{\hbar^2}{2I} j(j+1) \ , \qquad j = 0, 1, 2, ...,$$

   with degeneracy $2j + 1$. Write down the rotational contribution $Z^{(q)}_{\text{rot}}$ to the quantum partition function of one gas molecule. Approximate the formula for high temperatures and recover the classical result computed in (a). What does high temperature mean here?

   (c) Derive the low temperature limit of the quantum rotational partition function $Z^{(q)}_{\text{rot}}$. What is the physical interpretation of this result?

   (d) The vibrational modes are described by a 1-dimensional harmonic oscillator, which quantum-mechanically has energy levels

   $$E_n = \hbar\omega(n + \frac{1}{2}) \ , \qquad n = 0, 1, 2, ...$$

   Calculate the vibrational contribution $Z^{(q)}_{\text{vib}}$ to the quantum partition function of a single gas molecule, and find the leading order approximation in the high temperature limit (which coincides with the classical result). What does high temperature mean here?

   (e) Derive the leading term of Z_{vib} in the low temperature limit. What is the physical interpretation of this result?

10. Consider a quantum system where single particles have a discrete spectrum of states $|r\rangle$ with energies E_r. The particles satisfy *parastatistics*: each energy level can be occupied by at most p particles.

    (a) Which values of p correspond to bosons and fermions respectively?

    (b) Write down the grand canonical partition function $\mathcal{Z}_r$ for the single state $|r\rangle$ and express it in terms of $x_r = \exp[-\beta(E_r - \mu)]$.

    (c) Write down the full grand canonical partition function $\mathcal{Z}$ and compute the average number of particles $\langle N \rangle$.

    (d) Derive a formula for the average number of particles $\langle n_r \rangle$ that occupy state $|r\rangle$ and check that $\langle N \rangle = \sum_r \langle n_r \rangle$.
    Substitute into the formula for $\langle n_r \rangle$ the values of p appropriate for fermions and bosons and recover the standard formulae for the Fermi-Dirac and the Bose-Einstein distributions. (To recover the result for bosons, assume that $\mu < E_r$ for all r.)

SECTION C

11. (a) Define the following terms:

    i. Phase transition and 2nd order phase transition;
    ii. Latent heat;
    iii. Triple point;
    iv. Critical exponent.

    (b) Consider a Ginzburg-Landau mean field theory with zero external field $h = 0$ and potential

$$W(m) = \frac{1}{2} b\, t\, m^2 + \frac{1}{4} u\, m^4$$

    for the constant mean field $\phi(x) = m$ of the order parameter density. Here b and u are positive constants, and $t = (T - T_c)/T_c$ where T_c is the critical temperature.

    i. Plot the potential $W(m)$ and determine whether or not the $m \leftrightarrow -m$ symmetry is spontaneously broken for $T > T_c$ and for $T < T_c$.
    ii. By minimizing the free energy, compute the value of the mean field and determine the critical exponent for the order parameter.