Durham
University

EXAMINATION PAPER

Examination Session: May	**Year:** 2019	**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:	

Useful formulae:

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

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

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

- Dirac delta function:

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

SECTION A

1. The energy fundamental relation expresses the internal energy E of a system in terms of the other extensive quantities like the entropy S, the volume V and the number of particles N. Consider a system whose energy fundamental relation is

$$E(S, V, N) = \alpha\, S^a V^{-b} N^c \ ,$$

for some positive constant α.

   (a) Find the condition on the parameters $\{a, b, c\}$ for which the above energy fundamental relation is acceptable.

   (b) Find the temperature $T = T(S, V, N)$ and determine the condition on the parameters $\{a, b, c\}$ which ensures that the 3rd Law of Thermodynamics is upheld.

   (c) Write down the enthalpy $H(S, p, N)$ of the system.

2. The internal energy of a fluid is a function $E(S, V, N)$ of its entropy S, volume V and number of particles N.

   (a) Write down an expression for the differential dE according to the 1st Law of Thermodynamics.

   (b) Perform a double Legendre transform with respect to the pairs of conjugate variables (S, T) and (N, μ) to define the grand canonical potential $\Phi(T, V, \mu)$, and compute its differential $d\Phi$.

   (c) Express the entropy S, the pressure p and the number of particles N in terms of the temperature T, the volume V and the chemical potential μ.

   (d) Use the extensivity of the grand canonical potential to deduce that

$$\Phi(T, V, \mu) = -p(T, \mu)V \ .$$

3. The probability density for the speed of non-interacting monatomic gas particles moving in two spatial dimensions is given by the Rayleigh distribution:

$$p(v) = \frac{1}{\mathcal{N}}\, v \exp\left(-\frac{v^2}{2a^2}\right) \ , \qquad a^2 = k_B T/m \ . \tag{1}$$

The speed $v = |\boldsymbol{v}|$ is the the modulus of the velocity vector $\boldsymbol{v}$, and $\mathcal{N}$ is a normalization constant.

   (a) Determine $\mathcal{N}$ so that the probability distribution is correctly normalized.

   (b) Compute the mean $\langle v \rangle$ and the variance σ_v^2 of this probability distribution.

   (c) Compute the average energy of a gas particle. Is the result consistent with the equipartition theorem?

   (d) Find the probability density $p_E(E)$ for the energy of a gas particle.

4. (a) Define the canonical partition function for a quantum system maintained at a fixed temperature T. How is it related to the probability distribution for the canonical ensemble?

   (b) Consider a classical system of N identical non-interacting particles confined in a volume V in three dimensions. Compute the canonical partition function and calculate the mean energy $\langle E\rangle$, the free energy F and the entropy S of the system in the limit where N is large.

5. (a) Define the density of states $g(E)$ of a system. Write a formula for the exact density of states $g(E)$ of a quantum-mechanical system with energy eigenstates $|n\rangle$ and energy eigenvalues E_n, and use it to express the canonical partition function of the system as an integral over the energies.

   (b) A quantum-mechanical rotor with moment of inertia I has a Hamiltonian $\hat{H}$ with eigenvalues and eigenstates given by

$$\hat{H}|j,m_j\rangle = \frac{\hbar^2}{2I}j(j+1)|j,m_j\rangle \equiv E_{j,m_j}|j,m_j\rangle$$

   where $j = 0,1,2,3,\ldots$ and $m_j = -j,-j+1,\ldots,j-1,j$. Write an exact formula for its density of states $g(E)$, and show that it is approximated by the density of states

$$g_{\rm c}(E) = \begin{cases} 0\ , & E<0 \\ 2I/\hbar^2\ , & E>0 \end{cases}$$

   for energies such that $|E| \gg \hbar/\sqrt{I}$.

6. Consider a quantum system of N non-interacting bosons, where each boson can occupy one of the discrete one-particle states $|r\rangle$ of energy E_r. The ground state $|0\rangle$ has zero energy $E_0 = 0$.

   (a) Write down the Bose-Einstein distribution for the average number of bosons $\langle n_r\rangle$ that occupy state $|r\rangle$. For which range of the chemical potential μ and of the fugacity $z = e^{\beta\mu}$ is the formula sensible?

   (b) Approximate the Bose-Einstein distribution for $z \ll 1$, which turns out to be a high temperature limit, to derive the classical Maxwell-Boltzmann statistics.

   (c) Analyse the expected number $\langle n_0\rangle$ of bosons in the ground state in the limit where z is very close to 1. Taking into account that the system consists of a finite (though very large) number N of bosons, can z get arbitrarily close to 1? If not, estimate the maximum value of z that can be physically realised, as a function of $N \gg 1$.

SECTION B

7. Consider a gas with a fixed number of constituents N (that is omitted in the following).

   (a) Starting from the exact differentials of the thermodynamic potentials $E(S,V)$, $F(T,V)$, $G(T,p)$ and $H(S,p)$, derive the four Maxwell relations for the partial derivatives of S, T, V and p.

   (b) Derive the identities

$$\left.\frac{\partial S}{\partial T}\right|_p = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_p , \qquad \left.\frac{\partial S}{\partial p}\right|_T = \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial p}\right|_T .$$

   (c) Show that if three variables x, y and z satisfy a constraint $f(x,y,z)=0$ for all x, y and z, then

$$\left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1 .$$

   (d) Express the heat capacities at constant volume C_V and at constant pressure C_p in terms of derivatives of the entropy for reversible processes. Show that:

$$\begin{aligned} C_p - C_V &= T\left.\frac{\partial V}{\partial T}\right|_p \left.\frac{\partial p}{\partial T}\right|_V = -T\left.\frac{\partial V}{\partial T}\right|_p^2 \left.\frac{\partial p}{\partial V}\right|_T , \\ \left.\frac{\partial E}{\partial V}\right|_T &= T\left.\frac{\partial p}{\partial T}\right|_V - p , \\ \left.\frac{\partial C_V}{\partial V}\right|_T &= T\left.\frac{\partial^2 p}{\partial T^2}\right|_V . \end{aligned}$$

8. An isolated system consists of a fixed number N of non-interacting quantum particles, which are located at different positions in space and are therefore distinguishable. Each particle can sit in either of two states: the ground state $|0\rangle$ or the excited state $|1\rangle$, which have energies $\epsilon_0 = 0$ and $\epsilon_1 = \epsilon$ respectively.

   (a) Which quantities specify a macrostate of the system? Express these quantities in terms of ϵ and of the occupation numbers N_0 and N_1 which count how many particles sit in the ground state and in the excited state respectively.

   (b) Which quantities specify a microstate of the system? Relate the quantities that specify a microstate to the quantities that specify the macrostate.

   (c) Derive a general formula for the number of microstates that realizes a given macrostate of the system, and write the discrete probability distribution for a microstate in the appropriate statistical ensemble.

   (d) Compute the entropy $S(E, N)$ of the system and approximate it using Stirling's formula in the thermodynamic limit of large N and E. Rewrite the result in terms of $x_i = N_i/N$ $(i = 0, 1)$, the "filling fractions" for the two states.

   (e) Compute the temperature $T(E, N)$ as a function of the energy E and the number of particles N. Invert the formula to express the energy $E(T, N)$ in terms of the temperature T and the number of particles N.

   (f) Analyse the low temperature and the high temperature limits of the energy: how are the two states occupied in these two limits?

9. Let us examine the thermodynamics of an anharmonic oscillator in one dimension.

   (a) First consider a classical anharmonic oscillator whose Hamiltonian is

$$H(q,p) = \frac{p^2}{2m} + aq^2 + bq^4 \ ,$$

   where a and b are positive numbers. Calculate the canonical partition function and from it the heat capacity at constant volume for a system of N non-interacting indistinguishable anharmonic oscillators. You should work in the approximation where the anharmonicity is small, that is you can assume that $b/a^2 \ll 1$ and derive your results to leading order in this small parameter.

   (b) Now consider the quantum version of the above. The energy spectrum of a single oscillator is given to be

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega + x\left(n + \frac{1}{2}\right)^2 \hbar\omega \ , \qquad n = 0, 1, 2, \ldots$$

   Compute the grand canonical partition function of this system, correct to leading order in the small parameter x which now measures the anharmonicity. You may use the formula

$$\frac{d^2}{dy^2}\frac{1}{2\sinh\frac{y}{2}} = \frac{3 + \cosh y}{16\sinh^3\frac{y}{2}} \ .$$

10. An ideal non-relativistic Fermi gas confined to a volume V is described by the grand canonical partition function

$$\mathcal{Z} \equiv e^{-\beta\Phi} = \prod_r (1 + ze^{-\beta E_r}) \ , \qquad z = e^{\beta\mu} \ ,$$

where r labels the one-particle states (of energies E_r) available to a single fermion and μ is the chemical potential.

(a) Ignoring any internal degrees of freedom, such as spin, and assuming that the energy levels are almost continuous, $E_r \approx \hbar^2 \boldsymbol{k}^2/(2m)$, so that a sum over one-particle states can be approximated by an integral

$$\sum_r \approx \frac{V}{(2\pi)^3} \int d^3\boldsymbol{k} \ ,$$

show that the mean particle number $\langle N \rangle$ of the system can be written as

$$\langle N \rangle = V\lambda^3 f_{3/2}(z)$$

where λ is a constant that you should determine and

$$f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \ \frac{x^{\nu-1}}{z^{-1}e^x + 1} \ .$$

(b) Show that the mean energy is similarly given by

$$\langle E \rangle = \frac{3}{2} \frac{V\lambda^3}{\beta} f_{5/2}(z) \ .$$

(c) Using the following approximations, valid for large z,

$$f_{3/2}(z) \approx \frac{4(\ln z)^{3/2}}{3\sqrt{\pi}} \left(1 + \frac{\pi^2}{8(\ln z)^2}\right) , \quad f_{5/2}(z) \approx \frac{8(\ln z)^{5/2}}{15\sqrt{\pi}} \left(1 + \frac{5\pi^2}{8(\ln z)^2}\right) ,$$

show that at low temperatures

$$\frac{\langle E \rangle}{\langle N \rangle} \approx \frac{3}{5} E_F (1 + O(1/\beta^2)) \ ,$$

where the Fermi energy E_F is to be determined in terms of the average number of particles $\langle N \rangle$ and the volume V.

SECTION C

11. The Ising chain consists of a set of N spins s_i, $i = 1, 2, ..., N$, which can take the values ± 1 and are equally spaced on a one-dimensional periodic (*i.e.* circular) lattice. The energy for a particular configuration of spins $\{s_i\}$ is given by

$$E[\{s_i\}] = -J \sum_{i=1}^{N} s_i s_{i+1} - \frac{B}{2} \sum_{i=1}^{N} (s_i + s_{i+1}) \ ,$$

where we impose the periodic boundary condition $s_{N+1} \equiv s_1$. Here B is the external magnetic field (rescaled by the dipole moment) and J is a coupling constant that is assumed to be positive.

(a) Briefly describe the effect on the spins of the two contributions to the energy.

(b) Write down the canonical partition function Z_N for the system, and prove that

$$Z_N = \mathrm{tr}(T^N) \ ,$$

where T is the 2×2 transfer matrix

$$T = \begin{pmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{pmatrix} \ .$$

Express the partition function in terms of the eigenvalues of the transfer matrix, which you should determine.

(c) Assuming that $N \gg 1$, find an estimate for the partition function and the average magnetization $m = \sum_{i=1}^{N} \langle s_i \rangle$ of the system.

(d) Does the system exhibit spontaneous magnetization, that is a non-vanishing average magnetization at low temperatures in the absence of a magnetic field? Briefly discuss the physical interpretation of this fact.