

Candidate number:
Desk number:

King's College London

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B.Sc. EXAMINATION

6CCP3212 Statistical Mechanics

Examiner: Dr Eugene Lim

**Examination Period 2
(Summer 2019)**

Time allowed: THREE hours

Candidates may answer as many parts as they wish from SECTION A, but the total mark for this section will be capped at 40.

Candidates should also answer TWO questions from SECTION B. No credit will be given for answering a further question from this section. The approximate mark for each part of a question is indicated in square brackets.

Calculators may be used. The following models are permitted: Casio fx83 and Casio fx85.

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Physical Constants

Permittivity of free space	$\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$
Speed of light in free space	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Gravitational constant	$G = 6.673 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$
Elementary charge	$e = 1.602 \times 10^{-19} \text{ C}$
Electron rest mass	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Unified atomic mass unit	$m_u = 1.661 \times 10^{-27} \text{ kg} = 931.494 \text{ MeV } c^{-2}$
Proton rest mass	$m_p = 1.673 \times 10^{-27} \text{ kg}$
Neutron rest mass	$m_n = 1.675 \times 10^{-27} \text{ kg}$
Planck constant	$h = 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} = 8.617 \times 10^{-11} \text{ MeV K}^{-1}$
Stefan-Boltzmann constant	$\sigma = 5.670 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Avogadro constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Molar volume of ideal gas at STP	$= 2.241 \times 10^{-2} \text{ m}^3$
One standard atmosphere	$P_0 = 1.013 \times 10^5 \text{ N m}^{-2}$

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Useful Information

Maxwell Relations

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V,$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \quad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S.$$

Fundamental Equation of Thermodynamics

$$dE = TdS - PdV + \mu dN$$

Thermodynamic Potentials

$$F = E - TS, \quad \Phi = E - TS + PV, \quad H = E + PV.$$

with differentials

$$dF = -SdT - PdV + \mu dN, \quad d\Phi = -SdT + VdP + \mu dN, \quad dH = TdS + VdP + \mu dN.$$

Heat Capacities

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V, \quad C_P = T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

Microcanonical Ensemble Entropy

$$S = k_b \ln \Omega$$

Canonical Partition Function and formulas

$$Z = \sum_r e^{-\beta E_r}, \quad P_r = \frac{1}{Z} e^{-\beta E_r}, \quad \langle X \rangle = \sum_r P_r X_r,$$

$$F = -k_b T \ln Z, \quad S = k_b \frac{\partial}{\partial T} (T \ln Z), \quad \text{Mean Energy } \langle E \rangle = - \left(\frac{\partial \ln Z}{\partial \beta} \right)$$

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Grand Canonical Ensemble Partition Function

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)} ,$$

Mean Energy $\langle E \rangle = - \left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right) + \mu \langle N \rangle$, Mean Particle Number $\langle N \rangle = \frac{1}{\beta} \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)$.

Fermi-Dirac Distribution

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} + 1} .$$

Bose-Einstein Distribution

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} - 1} .$$

Thermal de Broglie wavelength

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_bT}} .$$

Stirling's Formula

$$\ln N! = N \ln N - N .$$

Polylog integrals

$$\int_0^\infty \frac{x^{n-1}}{e^x + 1} dx = (1 - 2^{1-n})\Gamma(n)\zeta(n) , \quad (n > 0),$$

and

$$\int_0^\infty \frac{x^{n-1}}{e^x - 1} dx = \Gamma(n)\zeta(n) , \quad (n > 1),$$

with Riemann Zeta function

$$\zeta(p) \equiv \sum_{n=1}^{\infty} \frac{1}{n^p} ,$$

and the Gamma function

$$\Gamma(n) \equiv \int_0^\infty x^{n-1} e^{-x} dx .$$

The Gamma function for $n > 0$ integers is

$$\Gamma(n) = (n - 1)! , \quad n \in \mathcal{N} - \{0\} .$$

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Common values for half-integer Gamma functions

$$\Gamma(1/2) = \sqrt{\pi} , \Gamma(3/2) = \frac{\sqrt{\pi}}{2} , \Gamma(5/2) = \frac{3\sqrt{\pi}}{4} , \Gamma(7/2) = \frac{15\sqrt{\pi}}{8} .$$

and Zeta functions

$$\zeta(3/2) = 2.612 , \zeta(2) = \frac{\pi^2}{6} , \zeta(5/2) = 1.341 , \zeta(3) = 1.202 , \zeta(7/2) = 1.127 .$$

Gaussian Integral

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

Geometric Sum

$$\sum_{n=0}^{n=\infty} x^n = \frac{1}{1-x} , |x| < 1 .$$

A derivative identity between x , y and z with a single constraint $x(y, z)$

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

Differential transform from $f(x, y) \rightarrow f(x, z)$ for a function $f(x, y)$ with a constraint $x = x(y, z)$

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z .$$

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SECTION A

Answer SECTION A in an answer book.

Answer as many parts of this section as you wish. Your total mark for this section will be capped at 40.

1.1 State the Zeroth and 1st laws of Classical Thermodynamics.

[3 marks]

1.2 What is the *statistical weight* of an ensemble?

[3 marks]

1.3 State which of the following are exact differentials. Integrate the equation if it is exact.

(i) $dG(x, y, z) = yzdx + zx dy + xydz.$

(ii) $dG(x, y) = 2xe^{-y}dx - x^2e^{-y}dy.$

(iii) $dG(x, y) = (3x^2 + y)dx + 2ydy.$

[9 marks]

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1.4 Suppose X and Y are *extensive* variables. Show that this implies that X/Y is an *intensive* variable.

[6 marks]

1.5 The free energy of blackbody radiation is given by

$$F = -\frac{V\pi^2(k_bT)^4}{45(\hbar c)^3},$$

where V and T are the volume and temperature. Prove that the energy density $\rho \propto T^4$.

[8 marks]

1.6 Consider a thermodynamic system with state variables P , T and V , related by some equation of state $P(V, T)$. By performing a coordinate transform from $S(P, T) \rightarrow S(T, V)$, show that

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial S}{\partial P}\right)_T + \left(\frac{\partial S}{\partial T}\right)_P.$$

You may use any formula provided.

[6 marks]

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- 1.7 A lattice has 5 possible sites, each with a magnetic dipole with two possible spin states, + and -. An energy of a + state has energy ϵ while the energy of a - state has energy $-\epsilon$. The total energy of the system is held by an external magnetic field such that $E = \epsilon$. What kind of statistical ensemble does this represent? Calculate the statistical weight of this system.

[8 marks]

- 1.8 The Maxwell-Boltzmann distribution of a gas at temperature T is given by

$$f(v)e^{-mv^2/2k_bT} = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} v^2 e^{-mv^2/2k_bT} ,$$

where the absolute velocity is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} .$$

Suppose the particles of the gas is *non-relativistic*, argue that the distribution in terms of energy E is

$$f(E)e^{-E/k_bT} = \sqrt{\frac{8}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} \frac{E}{m} e^{-E/k_bT} .$$

Prove that the most likely energy state of each gas particle is $E_{max} = k_bT$.

[8 marks]

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1.9 The Landau functional for a first order phase transition is given by

$$F = F_0(T) = a(T)m^2 + jm^3 + bm^4 ,$$

with

$$a(T) = \alpha(T) = \alpha(T - T_c) + \frac{9j^2}{32b} \quad (1)$$

with $\alpha > 0$, $b > 0$ and $j < 0$ being real constants. Find the equilibrium points of F as a function of the order parameter m . Show that when $T > T_c$, there are only one equilibrium point. Is this equilibrium point stable or unstable?

[9 marks]B

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SECTION B - Answer TWO questions
Answer SECTION B in an answer book

- 2) Consider an analog of the Van der Waals equation of state for a *diatomic* gas as follows

$$P = \frac{Nk_bT}{V-b} + \frac{N^2}{V^2}a \quad (2)$$

where $a > 0$ and $b > 0$ are constants. The + sign for the a term in the above equation means that the gas has *long range repulsive forces* instead of long range attractive forces for the standard Van der Waals gas.

- (a) State the conditions for a system to be in a *critical point*.

[2 marks]

- (b) Does the gas described by the equation of state above possess a critical point? If so, find T_c , P_c and V_c as functions of N , a and b . If not, prove it.

[6 marks]

- (c) The energy E of any system is given by

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V .$$

In the limit of very low densities and room temperature, it is found experimentally that the heat capacity of this gas is $C_V = 5/2Nk_b$. Show that the energy E of the system is given by

$$E(T, V) = \frac{5}{2}Nk_bT + \frac{aN^2}{V} .$$

[10 marks]

- (d) For a gas of fixed N , and using the fundamental equation of thermodynamics, show that

$$dS = \frac{5}{2}Nk_b \frac{dT}{T} + \frac{Nk_b}{V-b} dV .$$

[6 marks]

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(e) The isothermal compressibility of a gas is given by

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T .$$

Calculate K_T for this gas. Show that as $V \rightarrow \infty$, $\lim_{V \rightarrow \infty} K_T \rightarrow 1/P$.

[6 marks]

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- 3) Consider a gas of ideal non-relativistic fermions of spin-1/2 and mass m_F , trapped on a 2 dimensional surface of area A . For these quantum particles, the energy is given by

$$E_{\mathbf{n}} = \frac{\hbar^2 k^2}{2m_F} = \frac{4\pi^2 \hbar^2}{2m_F a^2} (n_x^2 + n_y^2), \quad k = \sqrt{k_x^2 + k_y^2},$$

where $n_x, n_y = 0, 1, 2, 3, \dots$ label the possible quantum numbers, and $n_i = ak_i/(2\pi)$.

- (a) By converting the sum into an integral

$$\sum_{\mathbf{n}} \rightarrow \int dn_x dn_y,$$

show that the density of states $g(E)$ is given by

$$g(E) = \tilde{g} \frac{2\pi m_F A}{(2\pi\hbar)^2},$$

where $\tilde{g} = 2$ for spin-1/2 fermions.

[6 marks]

- (b) The *fugacity* of a species of particle with chemical potential μ is defined to be

$$z \equiv e^{\beta\mu}.$$

Show that the number density n_F of the fermions on this two dimensional plane is given by

$$n_F \equiv \frac{\langle N \rangle}{A} = \tilde{g} \lambda_F^{-2} \ln(1 + z),$$

where $\lambda = \sqrt{2\pi\hbar^2/m_F k_b T}$ is the thermal de Broglie wavelength.

(*Hint*: You may find the following integral

$$\int_0^\infty \frac{dx}{\alpha^{-1} e^x \pm 1} = \pm \ln(1 \pm \alpha),$$

for any real constant a useful.)

[6 marks]

QUESTION CONTINUES ON NEXT PAGE

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- (c) Repeat the calculation for part (b), but this time for a gas of spin-0 *bosons* of mass m_B . Show that the number density of bosons is given by

$$n_B \lambda_B^2 = -\ln(1 - z_B) , \quad (3)$$

where z_B is the fugacity of the boson, and $\lambda_B = \sqrt{2\pi\hbar^2/m_B k_b T}$.

[2 marks]

- (d) At some sufficiently low temperature T_* , the fermions are non-interacting with the exception that opposite spin fermions can pair up to form spin-0 bosons of mass $m_B = 2m_F$, with interaction energy Δ , such that the energy of each boson is given by

$$E_B = -\Delta + \frac{\hbar^2 k^2}{2m_B} ,$$

with chemical potential $\mu_B \equiv 2\mu$. At equilibrium with temperature T , due to the reactions n_F and n_B are not conserved, but the *total number density* $n = n_F + 2n_B$ is conserved. Show that

$$n \lambda_F^2 = 2 \ln(1 + z) - 4 \ln(1 - z^2 e^{\beta\Delta}) . \quad (4)$$

[8 marks]

- (e) Prove that in the limit $n \lambda_F^2 \gg 1$, almost all the fermions are paired up into bosons, i.e.

$$n_B \approx \frac{1}{2} n .$$

[8 marks]

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4) A system consists of two identical, non-interacting, spin-less particles. The system has only 3 single particle states, labeled 1, 2 and 3, with energies $\epsilon_1 = 0 < \epsilon_2 < \epsilon_3$ respectively.

(a) Define what is meant by a *microcanonical ensemble* and a *canonical ensemble*.

[4 marks]

(b) Write down all the possible states and their total energies for the above system if the particles are (i) fermions and (ii) bosons.

[8 marks]

(c) Write down the partition function for a canonical ensemble at temperature $T = 1/k_b\beta$, for both the fermionic and bosonic cases of part (b).

[4 marks]

(d) In the low temperature limit $\beta\epsilon_3 \gg 1$, we can neglect all but the first two leading order terms of the partition functions derived in part (c). Compute the mean energy densities of the fermionic system $\langle E_F \rangle$ and of the bosonic system $\langle E_B \rangle$ respectively.

[8 marks]

(e) What are the mean energies of these systems in the limit as $T \rightarrow 0$? Discuss this results in the context of the symmetric/anti-symmetric properties of bosonic/fermionic wavefunctions.

[6 marks]