King's College London

B.Sc. EXAMINATION

6CCP3212 Statistical Mechanics

Examiner: Eugene Lim

Examination Period 1
(January 2023)

Time allowed: THREE hours

Candidates should answer all parts of SECTION A, which provides 40 marks out of a total of 100 for the whole paper.

Candidates should also answer BOTH questions from SECTION B. 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.

DO NOT REMOVE THIS EXAM PAPER
FROM THE EXAMINATION ROOM

TURN OVER WHEN INSTRUCTED

Physical Constants

Permittivity of free space	$\epsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7}$ H m^{-1}
Speed of light in free space	c $= 2.998 \times 10^{8}$ m s^{-1}
Gravitational constant	G $= 6.673 \times 10^{-11}$ N m^{2} kg^{-2}
Elementary charge	e $= 1.602 \times 10^{-19}$ C
Electron rest mass	$m_{\mathrm{e}} = 9.109 \times 10^{-31}$ kg
Unified atomic mass unit	$m_{\mathrm{u}} = 1.661 \times 10^{-27}$ kg $= 931.494$ MeV c^{-2}
Proton rest mass	$m_{\mathrm{p}} = 1.673 \times 10^{-27}$ kg
Neutron rest mass	$m_{\mathrm{n}} = 1.675 \times 10^{-27}$ kg
Planck constant	$\hbar = 1.055 \times 10^{-34}$ J s
Boltzmann constant	$k_{\mathrm{B}} = 1.381 \times 10^{-23}$ J K^{-1} $= 8.617 \times 10^{-11}$ MeV K^{-1}
Stefan-Boltzmann constant	$\sigma = 5.670 \times 10^{-8}$ W m^{-2} K^{-4}
Gas constant	$R = 8.314$ J mol^{-1} K^{-1}
Avogadro constant	$N_{\mathrm{A}} = 6.022 \times 10^{23}$ mol^{-1}
Molar volume of ideal gas at STP	$= 2.241 \times 10^{-2}$ m^{3}
One standard atmosphere	$P_0 = 1.013 \times 10^{5}$ N m^{-2}

Useful Information

Maxwell Relations

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

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

Fundamental Equation of Thermodynamics

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

Thermodynamic Potentials

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

with differentials

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

Heat Capacities

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

Microcanonical Ensemble Entropy

$$S = k_b \ln \Omega$$

Canonical Partition Function and formulas

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

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

Grand Canonical Ensemble Partition Function

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

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

$$\ln N! \approx N\ln N - N \ , \ N \gg 1$$

Polylog integrals

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

and

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

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

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

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 $f(x, y) \to f(x, z)$ for a function $f(x, y)$ with a constraint $x = x(y, z)$

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

SEE NEXT PAGE

SECTION A

Answer all parts of this section.

1.1 (i) State the *postulate of equal a priori probability.*

(ii) State what is an *isolated system.*

[6 marks] [B]

1.2 State which of the following differentials are exact and which are inexact. Find $F(x, y)$ if exact. Find $F(x, y)$

(i) $dF = (e^x y^2 + e^x xy^2)dx + (2e^x xy)dy$

(ii) $dF = (x + y^2)^{-1}dx + 2y(x + y^2)dy$

(iii) $dF = y^2 dx - xy^{-3}dy$

[8 marks] [P]

1.3 A thermodynamic system has a 2 dimensional state space,

(i) Define what is meant by *intensive* and *extensive* variables.

(ii) Suppose a function of state can be described by an intensive function $F(b, Y, Z) = bY/Z$, where Y and Z are extensive variables. Argue that b must be an intensive variable.

[6 marks] [B]

1.4 A system of 4 non-interacting and distinguishable particles are trapped on a lattice, such that they can only occupy the three discrete energy states at $E = \epsilon, 2\epsilon, 3\epsilon$.

(i) What are the possible energies E of the system if the entropy is zero?

(ii) What is the entropy of the system if the energy $E = 10\epsilon$?

[6 marks]U

1.5 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

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

Calculate the mean inverse velocity $\langle v^{-1} \rangle$.

[6 marks]B

1.6 The energy or the Hamiltonian of a dynamical tri-atomic particle with each atom labeled $1, 2, 3$ is given by

$$H(\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3, q_{12}, q_{23}) = \frac{1}{2m}\mathbf{p}_1^2 + \frac{1}{2m}\mathbf{p}_2^2 + \frac{1}{2m}\mathbf{p}_3^2 + \frac{1}{2}\lambda q_{12}^2 + \frac{1}{4}\alpha q_{23}^4 ,$$

where m is the mass of the atoms; $\mathbf{p}_1$, $\mathbf{p}_2$ and $\mathbf{p}_3$ are the momenta of the atoms, λ and α are the interaction strengths; and q_{12} and q_{23} are the distance between particles 1-2, and 2-3 respectively.

Using the equipartition theorem or otherwise, calculate the mean energy $\langle E \rangle$ for this system in equilibrium.

[8 marks]B

SEE NEXT PAGE

Solutions A

1.1

(i) All microstates are equally probably at equilibrium. [3 marks]

(ii) A system which does not interact with its surroundings either through work or heat exchange. [3 marks]

1.2

(i) Exact $F(x,y) = e^x xy^2$. [3 marks]

(ii) Exact $F(x,y) = \log(x+y^2)$. [3 marks]

(iii) Inexact. [2 marks]

1.3

(i) Extensive variables scale with size $X \to aX$ while intensive variables don't scale with size $a \to a$. [3 marks]

(ii) Since F is intensive, it doesn't scale, if we scale $X \to aX$ and $Y \to aY$, then $b \to b$ to keep F intensive. [3 marks]

1.4

(i) For zero entropy, we need to find configurations of the energy where there is only one microstate. So we can have either all 4 particles occupying the ϵ state or the 3ϵ state, hence $E = 4\epsilon$ or $E = 12\epsilon$. [2 marks].

(ii) For $E = 10\epsilon$, we either have (a) 3 particles at 3ϵ and 1 particle at ϵ or (b) 2 particles at 3ϵ and 2 particles at 2ϵ. If we label (a,b,c,d) to be the energy in which particle a occupy etc, then (a) has $(1,3,3,3)$, $(3,1,3,3)$, $(3,3,1,3)$, $(3,3,3,1)$, i.e. ${}^4C_1$, while (b) has $(3,3,2,2)$, $(3,2,3,2)$, $(2,3,3,2)$, $(2,3,2,3)$, $(2,2,3,3)$, so for a total of 9 microstates. The entropy is then $S = k_b \log 9$. [4 marks]

1.5 Just integrate [6 marks]

$$\begin{aligned}
\langle v^{-1} \rangle &= \int_0^\infty v^{-1} f(v) e^{-mv^2/2k_bT} \\
&= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT}\right)^{3/2} \int_0^\infty v e^{-mv^2/2k_bT} dv \\
&= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT}\right)^{3/2} \left[-\frac{k_bTe^{-av^2}}{m}\right]_0^\infty \\
&= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT}\right)^{1/2} .
\end{aligned} \tag{1}$$

1.6 Using the equipartition theorem, the energies for the momenta is $3/2k_bT$ each [2 marks], for the first interaction $(1/2)\lambda q_{12}^2$ is $1/2k_bT$ [2 marks] and for the 2nd interaction $(1/4)\alpha q_{23}^4$ is $1/4k_bT$ [4 marks], for a total of $21/4k_bT$.

SEE NEXT PAGE

SECTION B - Answer BOTH questions

Answer all parts of this section.

B2)

(a) Consider a system of 4 *distinguishable* non-interacting spin-1/2 particles interacting with an externel magnetic field with strength B. Each particle can have spin of either $\uparrow$ or $\downarrow$, with energies $E_\uparrow = -mB$ and $E_\downarrow = mB$, where $+m$ and $-m$ are the magnetic dipole moment of a $\uparrow$ and a $\downarrow$ particle respectively. Suppose the energy of the system is $E_0 = 2mB$.

(i) Calculate the statistical weight of this system, $\Omega(E_0)$. Write down all the possible microstates.

[4 marks]UP

(ii) What is the probability that any given particle has spin $\downarrow$?

[2 marks]UP

(iii) Suppose we randomly pick two of the particles. We found that the first particle is $\downarrow$. What is the probability that the second particle has spin $\uparrow$? Explain your answer.

[4 marks]UP

(iv) Calculate the mean magnetic moment for this system, $\bar{\mu}$.

[3 marks]UP

QUESTION CONTINUES ON NEXT PAGE

SEE NEXT PAGE

(b)

A binary alloy consists of N_A of atoms type A and N_B of atoms type B, with a total number of atoms $N = N_A + N_B$. The atoms form a simple cubic lattice, each atom interacting only with its neighbours with interaction energy of J. The Landau functional for this system is approximated by

$$F = -Nk_bT\ln 2 + N\left(\frac{k_bT}{2} - 3J\right)x^2 + \frac{Nk_bT}{12}x^4,$$

where $x \equiv (N_A - N_B)/N$ denoting the *difference* fraction between the A and B atoms, is the *order parameter* of the system.

(i) Find the extrema of F. Show that at F turns over from being a minimum to a maximum at $x = 0$ at the critical temperature of $T_c = 6J/k_b$.

[8 marks]UP

(ii) Sketch the Landau functional F for the case $T > T_c$ and $T < T_c$.

[4 marks]UP

(iii) Describe what happens to the distribution of atoms A and B as the temperature is lowered from $T > T_c$ to $T < T_c$.

[5 marks]UP

SEE NEXT PAGE

Solution B2

B2 (a)

(i) The four possible microstates are $(\uparrow\downarrow\downarrow\downarrow)$, $(\downarrow\uparrow\downarrow\downarrow)$, $(\downarrow\downarrow\uparrow\downarrow)$, $(\downarrow\downarrow\downarrow\uparrow)$, i.e. $\Omega(2mB) = 4$. Can also note that since we must have 3 $\downarrow$ and 1 $\uparrow$, the number of configurations is $^4C_1$=4. [4 marks]

(ii) Since we must have 3 $\downarrow$ particles and 1 $\uparrow$ particle, the probability of any particles must have $\downarrow$ is simply $P_\downarrow = 3/4$. [2 marks]

(iii) WLOG, we can pick the first 2 particles of the configurations in (i). If particle 1 is $\downarrow$, then this restrict the number of microstates with this configuration to $(\downarrow\uparrow\downarrow\downarrow)$, $(\downarrow\downarrow\uparrow\downarrow)$, $(\downarrow\downarrow\downarrow\uparrow)$. [2 marks] The probability that particle 2 is $\uparrow$ is then $P = 1/3$. [2 marks].

(iv) From (ii), $P_\downarrow = 3/4$, thus $P_\uparrow = 1 - P_\downarrow = 1/4$. The mean magnetic moment of the system is then

$$\bar{\mu} = P_\uparrow \times (m) + P_\downarrow \times (-m) = -\frac{m}{2}. \tag{2}$$

[3 marks]

B2 (b)

(i) To find the extrema, differentiate w.r.t to x and set to zero

$$\frac{\partial F}{\partial x} = 2N\left(\frac{k_bT}{2} - 3J\right)x + \frac{Nk_bT}{3}x^3 = 0 \tag{3}$$

so the solutions are $x = 0$ and $x = \pm\sqrt{3}\sqrt{-\frac{6J}{k_bT} + 1}$. If $T > 6J/k_b$ then there is only one solution $x = 0$. [4 marks]

To find out if $x = 0$ is a minimum or maximum, we take the 2nd derivative

$$\frac{\partial^2 F}{\partial x^2} = N(k_bT - 6J) + Nk_bTx^2. \tag{4}$$

It's clear that this expression at $x = 0$ changes from positive to negative at the critical temperature $T_c = 6J/k_b$ as asserted. [4 marks]

(ii) Sketch. [4 marks]

(iii) At $T > T_c$, the only equilibrium point is at $x = 0$ since it is a minimum, meaning that the number of atoms $N_A = N_B$ wants to be equal. However, as we lower $T < T_c$, $x = 0$ becomes an unstable point, and a phase transition occurrs, with x falling into one of the two stable minima $x = \pm\sqrt{3}\sqrt{\frac{6J}{k_bT} - 1}$ – N_A or N_B will dominate the lattice. [5 marks]

SEE NEXT PAGE

B3)

(a) N number of *non-interacting* distinguishable diatomic molecules are restricted on a 2 dimensional surface which span the $x - y$ direction. Each molecule can be in one of the three possible microstate (a) aligned parallel to the surface along the x direction, (b) aligned parallel to the surface along the y direction and (c) aligned perpendicular to the surface z direction. If the molecule is aligned parallel to the surface, it has energy $E_x = E_y = 0$; while if it is aligned perpendicular to the surface, it has $E_z = \epsilon > 0$. The system is in thermal equilibrium at $T > 0$.

(i) What kind of statistical ensemble is this? Calculate the partition function Z for this system.

[5 marks]P

(ii) Calculate the mean energy for this system. Show that the maximum mean energy is $N\epsilon/3$. At what temperature is this limit achieved?

[5 marks]UP

(iii) What is the probability of a molecule being aligned perpendicular to the surface (i.e. in the z direction)?

[3 marks]P

(iv) Calculate the entropy S of the system as a function of ϵ, β and N. Show that the minimum S is not zero, and explain why this is so.

[5 marks]U

QUESTION CONTINUES ON NEXT PAGE

SEE NEXT PAGE

(b) Our universe is filled with the remnants of the radiation from the Big Bang called the *Cosmic Microwave Background*. This *blackbody* radiation is a bath of photons in thermal equilibrium at temperature $T \approx 3$ K today. Remember that each photon has two polarisation states, and the chemical potential for photons is $\mu = 0$, that the energy of a photon at frequency ω is given by $E_\omega = \hbar\omega$.

The density of states for a massless relativistic particle is given by

$$g(E)dE = \frac{4\pi V}{(2\pi\hbar)^3}\frac{E^2}{c^3}dE \ .$$

(i) Using the Bose-Einstein distribution, calculate the average photon *density* N/V in the universe in units of number per cm^3.

[6 marks]P

(ii) It is predicted that, in addition to the Cosmic Microwave Background, there exists a *Cosmic Neutrino Background* at around $T_\nu \approx 2$ K today Neutrinos are almost massless *fermions* and presently we believe that there are three species of neutrinos. Calculate the average neutrino *density* N_ν/V in the universe in units of number per cm^3. You can assume that neutrinos are massless, have zero chemical potential, and are relativistic.

[6 marks]U

FINAL PAGE

Solutions B3

(a)

(i) This is a canonical ensemble [1 mark]. The partition for a single system is $Z = 1 + 1 + e^{-\beta\epsilon} = 2 + e^{-\beta\epsilon}$ where $\beta = 1/k_bT$ [2 marks]. For N identical particles, it is then

$$Z_N = Z^N = (2 + e^{-\beta\epsilon})^N. \tag{5}$$

[2 marks]

(ii) The mean energy is [3 marks]

$$E = -\frac{\partial \log Z^N}{\partial \beta} = \frac{N\epsilon}{1 + 2e^{\beta\epsilon}} \tag{6}$$

Since $T > 0$ hence $\beta > 0$, then $e^{\beta\epsilon} \geq 1$. Thus $E \leq N\epsilon/3$, occuring when $\beta \to 0$ or when $T \to \infty$. [2 marks]

(iii) Since the molecules are not interacting, we can consider the subsystem of a single moelcule. The probability is then $P_z = (1/Z)e^{\beta\epsilon} = 1/(1 + 2e^{\beta\epsilon})$. [3 marks]

(iv) Using the formula for entropy

$$S = k_b(\log Z + \beta E) = k_b \left(N \log(2 + e^{-\beta\epsilon}) + \frac{\beta N\epsilon}{1 + 2e^{\beta\epsilon}} \right) \tag{7}$$

[3 marks]

For minimum entropy, $\beta \to \infty$, i.e. $T \to 0$, so $S_{min} = k_b N \log 2$. It is not zero since the ground state is degenerate in the x and y directions, hence it is $\propto \log 2$. [2 marks]

(b)

(i) The Bose-Einstein distribution is

$$\langle N_\omega \rangle = \frac{1}{e^{\frac{\hbar\omega}{k_bT}} - 1} \tag{8}$$

Then

$$\begin{aligned}
\langle N \rangle &= \sum_{\mathbf{n}} \frac{1}{e^{\beta E} - 1} \\
&= 2\int_0^\infty \frac{g(E)}{e^{\beta E} - 1} dE \\
&= 2\int_0^\infty \frac{4\pi V}{(2\pi\hbar)^3} \frac{E^2}{c^3} \frac{1}{e^{\beta E} - 1} dE \\
&= \frac{V}{\pi^2} \left(\frac{k_bT}{\hbar c} \right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx \\
&= \frac{V}{\pi^2} \left(\frac{k_bT}{\hbar c} \right)^3 \Gamma(3)\zeta(3)
\end{aligned} \tag{9}$$

[4 marks]. Plugging in all the numbers and being careful with units, one can then calculate that $\langle N \rangle / V \approx 1000$ cm^{-3}. [2 marks]

(ii) Since neutrinos as fermions, we use the Fermi-Dirac statistic [2 marks]

$$\langle N_\omega \rangle = \frac{1}{e^{\frac{E}{k_b T_\nu}} + 1} \tag{10}$$

Since neutrinos has 3 species vs 2 photon polarisation, and everything else remaining the same, we can immediately write down the final integral [2 marks]

$$\begin{aligned} \langle N \rangle &= \frac{3}{2} \frac{V}{\pi^2} \left(\frac{k_b T_\nu}{\hbar c} \right)^3 \int_0^\infty \frac{x^2}{e^x + 1} dx \\ &= \frac{3}{2} \frac{V}{\pi^2} \left(\frac{k_b T_\nu}{\hbar c} \right)^3 (1 - 2^{-2}) \Gamma(3) \zeta(3) \; . \end{aligned} \tag{11}$$

Plugging in the numbers again we get $\langle N_\nu \rangle / V \approx 350$ cm^{-3}. [2 marks]