King's College London

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B.Sc. EXAMINATION

6CCP3212 Statistical Mechanics

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Examination Period 1
(January 2024)

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.

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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

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

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

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

SECTION A

Answer all parts of this section.

1.1 Define each term you use carefully.

(i) What is meant by the *ergodic principle*?

(ii) What is a *diathermal walls*? Draw a diagram to illustrate your answer if needed.

(iii) What is a *canonical ensemble*?

[9 marks]

1.2 Which of the following differentials are exact and which are inexact? Find $F(x, y)$ if exact. Show your work clearly.

(i) $dF = (2x - yx^2)e^{-xy}dx - x^3e^{-xy}dy$

(ii) $dF = \frac{1}{y}dx$.

(iii) $dF = e^z dx + zdy + (xe^z + y)dz$.

(iv) $dF = \frac{\ln x}{xy}dx - \frac{\ln x}{y^2}dy$.

[10 marks]

1.3 A thermodynamic system has a 2 dimensional state space,

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

(ii) Suppose a function of state can be described by an extensive function $F(b, X, Y) = YXb$, where Y is an extensive variable and X is an intensive variables. Is b an extensive or intensive variable? Justify your answer.

[6 marks]

DNA is built from a sequence of bases which there are four types, A,T,G,C.

1.4 Consider the Shannon Entropy

$$S = -k_b \sum_r P_r \ln P_r \ .$$

(i) In natural DNA of primates, the four bases have nearly the same frequency $P(A) = P(T) = P(G) = P(C)$. Calculate the Shannon Entropy for the DNA of primates.

(ii) The DNA of bacteria on the other hand usually is more unbalanced in its distribution. Calculate the Shannon Entropy for the DNA snippet of a bacteria :

AACCTCGCGTCATCGATCTACACA.

[6 marks]

1.5

(i) Starting from $S(T, V)$, show that

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \ .$$

(ii) Using the result from (i), derive the following relationship

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

(iii) The equation of state of a gas can be written in the form

$$P = N k_b T (1 + B(T) N) \ ,$$

where $B(T)$ is a virial coefficient which depends on the temperature T. Using the results in (i) and (ii), calculate $(\partial E/\partial V)_T$ and show that it is positive as long as $\partial B/\partial T > 0$.

[9 marks]

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Solutions A

1.1

(i) The ergodic principle states that, given sufficient time [1 mark], all accessible phase space will be explored [2 mark].

(ii) Diathermal walls allow heat to be exchanged [2 marks] but not particles [1 mark].

(iii) The canonical ensemble is the subset of phase space [1 mark] for fixed V, N and T. [2 marks]

1.2

(i) Exact. $F = x^2 e^{-xy}$. [3 marks]

(ii) Inexact. [2 marks]

(iii) Exact. $F = xe^z + yz$. [3 marks]

(iv) Inexact. [2 marks]

1.3

(i) Extensive variables are those that scales with size while intensive variables don't. [2 marks]

(ii) If F is extensive, then F scales as $F \to aF$ [2 marks]. If Y is extensive and X is intensive, then under this scaling $F \to aYX(b')$, hence b' must not scale $b \to b'$, meaning that b is intensive. [2 marks]

1.4

(i) Sine they are equal in probabilities, $P = 1/4$ for all ACTG, thus $S = -k_b \sum (1/4) \ln(1/4) = k_b \ln 4$. [2 marks]

(ii) There are $7A$, $9C$, $5T$ and $3G$ for a total of 24 letters. The probabilities are then $P(A) = 7/24$, $P(C) = 9/24$, $P(T) = 5/24$ and $P(G) = 3/24$ [2 marks]. The entropy is then $S = 1.32k_b$. [2 marks]

1.5

(i) From $S(T, V)$, and

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{1}$$

[1 mark] and using (from rubric) $(\partial S/\partial T)_V = C_V/T$ and $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, we get the desired result. [2 mark]

(ii) Using the fundamental equation of thermodynamics, $dE = TdS - PdV$, we plug dS from (i) into it [1 mark], to get

$$dE = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \tag{2}$$

and the coefficient of the dV term is the desired result. [2 marks]

(iii) Plugging in the equation of state into the result in (ii), we get

$$\left(\frac{\partial E}{\partial V}\right)_T = N^2 k_b T \frac{\partial B}{\partial T} > 0 \tag{3}$$

since $N^2 > 0$, $k_b > 0$, $T > 0$ and $\partial B/\partial T > 0$ as given. [3 marks]

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SECTION B - Answer BOTH questions

Answer all parts of this section.

B2)

(a) Consider a single harmonic oscillator in 3 dimensions whose energy is given by

$$E = \frac{\mathbf{p}^2}{2m} + V(r) \ , \ V(r) = br^2 \ ,$$

where m is its mass, $b > 0$ is a constant and $V(r)$ is the potential centered at the origin with $r = \sqrt{x^2 + y^2 + z^2}$.

(i) Is the potential repulsive or attractive? Explain your answer.

[4 marks]

(ii) Calculate the partition function Z for this system, demonstrating that $Z \propto b^{-3/2}$.

[8 marks]

(iii) In the limit where $b \to 0$, using the result from (ii) seems to suggest that $Z \to \infty$. Is this physical? If so, justify your answer. If not, identify the correct way of taking this limit.

[2 marks]

(iv) Suppose the potential is changed such that the energy of the system is given by

$$E = \frac{\mathbf{p}^2}{2m} + br^{2n} \ ,$$

where $n > 1$ is an integer. By using spherical coordinates via the transform $\int_{-\infty}^{\infty} d^3\mathbf{x} = \int_0^{\infty} 4\pi r^2 dr$, calculate the partition function of this system.

[*Hint : one might find the integral representation of the Gamma function in the rubric useful.*]

[6 marks]

QUESTION CONTINUES ON NEXT PAGE

(b) Four non-interacting particles with mass m are confined to a cubic box of volume V with the energy E of each particle given by

$$E = \epsilon(n_x^2 + n_y^2 + n_z^2) \ , \ \epsilon > 0$$

where its quantum number n_x, n_y and n_z are non-zero positive integers. The *ground state* refers to the configuration where the energy of the system is minimum.

(i) Suppose the particles are *bosons*. What is the energy of the ground state E_0?

[3 marks]

(ii) Suppose the particles are *fermions*. What is the energy of the ground state E_0? Ignore spins.

[3 marks]

(iii) Assuming the system is a canonical ensemble, in the *classical limit*, the distinction between fermions and bosons becomes unimportant. Explain how the classical limit is achieved in the context of the system of 4 particles described above, and find the *approximate* condition as a function of ϵ. You may leave the answer as an inequality.

[4 marks]

Solution B2

B2 (a)

(i) Since $b > 0$, as we move away from the center $r \to \infty$ the energy E increases, and hence the probability of finding the particle $P \propto e^{-\beta E}$ decreases. Hence the potential is *attractive*. [4 marks]

(ii) The partition function is

$$Z = \frac{1}{(2\pi\hbar)^3} \int d^3\mathbf{x} d^3\mathbf{p} e^{-\beta\mathbf{p}^2/2m - \beta b r^2} \ . \tag{4}$$

The p and x integrals are separable and thus can be done independently using the gaussian integrals

$$\int d^3\mathbf{p} e^{-\beta\mathbf{p}^2/2m} = \left(\frac{2m\pi}{\beta}\right)^{3/2} \tag{5}$$

for p [3 marks] and

$$\int d^3\mathbf{x} e^{-\beta b(\mathbf{x}^2)} = \left(\frac{\pi}{\beta b}\right)^{3/2} \tag{6}$$

for x [3 marks]. Putting them together, we get

$$Z = \frac{1}{(2\pi\hbar)^3} \left(\frac{2m\pi^2}{\beta^2 b}\right)^{3/2} \tag{7}$$

[2 marks].

(iii) This is not the right way to take the limit since in the limit $b \to 0$, we approach the limit with no interactions and hence the partition function should reduce to that of the free particle $Z = V(m/2\pi\beta\hbar^2)^{3/2}$ which is finite. The right way to take the limit is to take $br^2 \ll k_b T$. [2 marks]

(iv) This is a slightly long calculation, but not too hard, just have to be careful.

The p integral is as in section (ii). The x integral is then, converting r into w via the transformation $w/(\beta b) = r^{2n}$ [1 marks], you get the integral

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-\beta b(r^{2n})} &= 4\pi \int_0^{\infty} r^2 e^{-\beta b(r^{2n})} dr \\ &= 4\pi \int_0^{\infty} \frac{1}{2n} \left(\frac{1}{\beta b}\right)^{3/2n} w^{\frac{3}{2n}-1} e^{-w} dw \end{aligned} \tag{8}$$

[2 marks]. This integral is a Gamma function, which yields

$$\frac{2\pi}{n} \Gamma\left(\frac{3}{2n}\right) \left(\frac{1}{\beta b}\right)^{3/2n} \ , \tag{9}$$

[2 marks]. Putting everything together we get the final answer

$$Z = \frac{1}{(2\pi\hbar)^3}\frac{2}{n}\pi^{5/2}\Gamma\left(\frac{3}{2n}\right)\left(\frac{2m\pi}{\beta}\right)^{3/2}\left(\frac{1}{b\beta}\right)^{3/2n} \tag{10}$$

. [1 mark]

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Solution (B2b)

(i) Since they are bosons, in their ground state, the quantum numbers for all the particles are $(1, 1, 1)$ [2 marks], so the ground state energy is $4 \times 3\epsilon = 12\epsilon$. [1 mark]

(ii) Since they are fermions, pauli exclusion means that the first 4 occupied states are $(1, 1, 1)$, $(1, 1, 2)$, $(1, 2, 1)$ and $(2, 1, 1)$ [2 marks]. This means that the ground state energy is $3\epsilon + 3 \times 6\epsilon = 21\epsilon$. [1 marks]

(iii) The classical limit is achieved when the temperature [1 mark] of the system is increased such that $k_b T_* \gg \epsilon$. In this limit, the mean energy of the system $\bar{E} \sim k_b T_* \gg \epsilon$ [1 mark], hence particles can occupy states with large (n_x, n_y, n_z) with a large degeneracy such that the pauli exclusion is no longer important [2 mark].

B3)

(a) Consider the problem of phase separation of a binary alloy consisting 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 with only 6 of its nearest neighbours. Each identical $A-A$ and $B-B$ pair interact attractively with interaction energy $-J$ while each alternate pair $A-B$ interact repulsively with energy $+J$, where $J > 0$.

(i) Argue that the *minimum energy configuration* of this alloy is where A atoms and B atoms *separate* into two different phases. Sketch the configuration.

[4 marks]

(ii) Show that the statistical weight Ω of the system is

$$\Omega = \frac{N!}{N_A! N_B!} \ .$$

[*Hint : You may find the formula* $^N C_M = N!/(M!(N-M)!)$ *useful.*]

[2 marks]

(iii) Using the result in (ii) and Stirling's approximation, calculate the entropy as a function of N, N_A and N_B.

[4 marks]

QUESTION CONTINUES ON NEXT PAGE

(iv) The *order parameter* $x \equiv (N_A - N_B)/N$ denotes the *difference* fraction between the A and B atoms. Using the order parameter, one can show that the Landau functional for this system is approximated by (you don't have to derive this)

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

Find the extrema of F and show that there is only one extrema when $T > T_c$ where the critical temperature $T_c \equiv 6J/k_b$.

[4 marks]

(v) Show that F turns over from being a minimum to a maximum at $x = 0$ at the critical temperature. Describe what happens to the distribution of atoms A and B as the temperature is lowered from $T > T_c$ to $T < T_c$.

[6 marks]

QUESTION CONTINUES ON NEXT PAGE

(b) Consider an isolated system of N distinct non-interacting particles. Each particle can be in any of the 3 possible energy levels with energies 0, ϵ, and 2ϵ respectively.

(i) In its *ground state*, which is the state of minimum energy, all the particles are in the energy level with zero energy such that the energy $E = 0$. What is the entropy S of the ground state?

[2 marks]

(ii) Suppose an amount of energy $\Delta E = \epsilon$ is added to the ground state. What is the entropy of this new system?

[2 marks]

(iii) Let the total energy of the system be $E = 2N\epsilon - \epsilon$. Argue that the entropy of the system is the same as that when $E = \epsilon$.

[3 marks]

(iv) Using the temperature definition $T^{-1} = \partial S/\partial E$, argue that the system described in (iii) is a system with *negative* temperature.

[3 marks]

FINAL PAGE

Solutions B3

(a)

(i) At the minimum energy configuration, since $A-B$ interaction is positive while $A-A$ and $B-B$ interaction energy is negative, we want a configuration which *minimize* the number of $A-B$ interactions [2 marks]. Hence the atoms A and B *separate* into two separate phases, touching only at a 2dimensional interface. [2 marks]

(ii) The total number of configuration is simply $\Omega = {}^N C_{N_A}$ (or $\Omega = {}^N C_{N_B}$), which immediately yields $\Omega = N!/(N_A!(N-N_A)! = N!/(N_A!N_B!)$. [2 marks]

(iii) This is a straightforward calculation. The entropy is $S = k_b \ln \Omega$ [1 marks], and using Stirling's approximation $\ln N! = N\ln N - N$, a little bit (really!) of algebra leads to [3 marks].

$$S = -Nk_b(P_A \ln P_A + P_B \ln P_B) \ ,$$

where $P_A = N_A/N$ and $P_B = N_B/N$.

(iv) To find the extrema, differentiate w.r.t to x and set to zero [1 marks]

$$\frac{\partial F}{\partial x} = 2N\left(\frac{k_bT}{2} - 3J\right)x + \frac{Nk_bT}{3}x^3 = 0 \tag{11}$$

so the solutions are $x = 0$ and $x = \pm\sqrt{3}\sqrt{-\frac{6J}{k_bT}+1}$ [2 marks]. If $T > 6J/k_b$ then there is only one solution $x = 0$. [1 marks]

(v) To find out if $x = 0$ is a minimum or maximum, we take the 2nd derivative [1 marks]

$$\frac{\partial^2 F}{\partial x^2} = N(k_bT - 6J) + Nk_bTx^2. \tag{12}$$

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. [2 marks]

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 occurs [1 mark], with x falling into one of the two stable minima $x = \pm\sqrt{3}\sqrt{\frac{6J}{k_bT} - 1}$ – either N_A or N_B will dominate the lattice. [2 marks]

(b)

(i) Since all the particles must be in the 0 energy level, there is only one possible configuration, hence the statistical weight is 1 so the entropy $S = k_b \ln \Omega = 0$. [2 marks]

(ii) If $E = \epsilon$, then one of the particles have energy ϵ while the rest has energy 0. There are N particles, so there are N possiblities, thus $S = k_b \ln N$. [2 marks]

(iii) This energy corresponds to the case where all the particles are in the 2ϵ level *except* one of them which is in the ϵ level. There are N particles, so there are N possiblities, yielding $S = k_b \ln N$ same as the case in (ii). [3 marks]

(iv) If we *add* $\Delta E = \epsilon > 0$ energy into the system in (iii), we get a total energy of $E = 2N\epsilon$, which means that all the particles are in the 2ϵ level. There is only one possible configuration, so $S = 0$, i.e. $\Delta S < 0$. Thus $\Delta S/\Delta E < 0$, implying that $T < 0$. [3 marks]