STATISTICAL MECHANICS K P N and A K K

PROBLEM SET - 1 9 January 2017

1.1 Starting from the first law of thermodynamics, show that a quasi-static reversible adiabatic process in an ideal gas is described by the relation,

- $PV^\gamma = \Theta_1$
- $TV^{\gamma-1} = \Theta_2$
- $P^{1-\gamma}T^\gamma = \Theta_3$

where $\Theta_i : i = 1, 2, 3$ are constants and $\gamma = C_P/C_V$. The value of γ for a mono atomic ideal gas is $5/3$.

1.2 Consider one mole of an ideal gas. A molecule of the gas is mono atomic and is spherically symmetric. The system of ideal gas is in equilibrium. Its temperature $T_1 = 300$ k and its volume $V_1 = 1$ litre. Since the system is in equilibrium, it can be represented by a point $A = (V_1, T_1)$, in the temperature-volume thermodynamic phase plane. We are taking Volume along the X axis and Temperature along the Y axis.

Now consider a process by which the system expands to a volume $V_2 = 2$ litres. The process is adiabatic.

Case-1 : The process is quasi static and reversible. Let T_2 be the temperature of the system at the end of the process. Let $B = (V_2, T_2)$ denote the system at the end of the process. **Find T_2**. The process $A \to B$ can be represented by a curve joining A to B. The curve is called an adiabat.

Case-2 : The process is not reversible. Hence the process can not be represented by a curve in the thermodynamic phase diagram. The system disappears from A at the start of the process. At the completion of the process, if we wait long enough, the system would equilibrate and appear at a point $B' = (T_2', V_2)$ in the phase diagram. There is no ready-made formula for calculating T_2'. Nor is there a formula for calculating the increase in entropy of the system in the irreversible process. Also these quantities depend on how far away the irreversible process is from its reversible companion. However B' is on a line parallel to Y axis and passing through B. Employing the Second law of thermodynamics

- find if the point B' is vertically above or below the point B.
- calculate the increase in entropy in terms of T_2'.

1

Hint : Consider a constant-volume, quasi static reversible process that takes the system from B' to B. Then take the system by a reversible adiabat from B to A and complete the cycle. The cyclic process,

$$A \rightarrow B' \rightarrow B \rightarrow A,$$

thus has three segments, one of them irreversible and the other two reversible.

- The segment $A \rightarrow B'$ is irreversible and adiabatic.
- The segments $B' \rightarrow B$ is reversible and occurs at constant volume.
- The segment $B \rightarrow A$ is reversible and adiabatic.

Employ the Second law for the cyclic process.

1.3 A Carnot engine operates between temperatures T_1 and T_2 ($< T_1$). Plot the Carnot cycle on Temperature-Entropy phase plane. Take S along the X axis and T along the Y axis. Employ this phase diagram and the first law of thermodynamics to show that the efficiency of a Carnot engine is given by,

$$\eta = \frac{W}{q_1} = 1 - \frac{T_2}{T_1}$$

where W is the work done by the engine during one cycle.

1.4 The step function is given by

$$\Theta(x) = \begin{cases} 0 & \text{for } x < 0 \\ \\ 1 & \text{for } x > 0 \end{cases}$$

Consider a function defined as,

$$f_\epsilon(x) = \begin{cases} 0 & \text{for } -\infty \leq x \leq -\dfrac{\epsilon}{2} \\ \\ \left(\dfrac{1}{\epsilon}\right) x + \dfrac{\epsilon}{2} & \text{for } -\dfrac{\epsilon}{2} \leq x \leq +\dfrac{\epsilon}{2} \\ \\ 1 & \text{for } +\dfrac{\epsilon}{2} \leq x \leq +\infty \end{cases}$$

It is easily verified that

$$\lim_{\epsilon \to 0} f_\epsilon(x) = \Theta(x).$$

The Dirac-delta function is defined as the derivative of the step function :

$$\delta(x) = \frac{d}{dx}\Theta(x) = \lim_{\epsilon \to 0} \frac{d}{dx} f_\epsilon(x)$$

Employing the above representation of the Dirac-delta function show that,

$$\int_{-\infty}^{+\infty} \delta(x) \, dx = 1$$

$$\int_{-\infty}^{+\infty} g(x) \, \delta(x - x_0) \, dx = g(x_0)$$

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PROBLEM SET - 2
16 January 2017

2.1 A thermally insulated chamber contains **1000** moles of mono-atomic ideal gas[1] at **10** atm. pressure. Its temperature is **300** K. The gas leaks out slowly through a valve into the atmosphere. The leaking process is quasi static, reversible and adiabatic[2].

  (i) How many moles of gas shall be left in the chamber eventually?

  (ii) What shall be the temperature of the gas left in the chamber ?

$$1 \text{ atm} = 0.981 \times 10^6 \text{ Pa} \; ; \gamma = \frac{C_P}{C_V} = \frac{5}{3} \; .$$

2.2 Palash Pal, *An Introductory Course of Statistical Mechanics*, Narosa (2008)p.4,exercise 4.1

The internal energy U (of a single component thermodynamic system) expressed as a function of entropy S, and volume V, is of the form

$$U(S, V) = a \; S^{4/3} V^\alpha,$$

where a and α are constants.

  (a) What is the value[3] of α ?

  (b) What is the temperature of the system ?

  (c) What is the pressure of the system ?

  (d) The pressure of the system obeys a relation given by

$$P = \omega U/V,$$

    where ω is a constant. Find the value of ω.

  (e) if the energy of the system is held constant, the pressure and volume are related by

$$PV^\gamma = \text{constant.}$$

    Find γ.

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[1] $PV = nRT$

[2] $PV^\gamma = \Theta$ where Θ is a constant.

[3] HINT : U, S, and V are extensive thermodynamic properties. Therefore U is a first order homogeneous function of S, and V. In other words $U(\lambda S, \lambda V) = \lambda U(S, V).$

2.3 Consider an isolated system of N identical, indistinguishable, and non-interacting point particles, in <u>two dimensions</u>. Each particle is of mass m. The particles are confined to an area A.

Let $\widehat{\Omega}(E, A, N)$ denote the number of micro states of the (macroscopic) system with energy less than or equal to E.

(i) Show that[4],

$$\widehat{\Omega}(E, A, N) = \frac{1}{h^{2N}} \frac{A^N}{N!} \frac{(2\pi m E)^N}{\Gamma(N+1)}$$

(ii) Derive an expression for the density of states of a single particle.

Carry out quantum-counting of micro states of a single particle confined to a two dimensional box of length L and

(iii) show that the resulting expression is the same as the one obtained by classical Boltzmann counting.

2.4 Consider an isolated system of N identical, indistinguishable, and non-interacting point particles, in <u>one dimension</u>. Each particle is of mass m. The particles are confined to a length L.

Let $\widehat{\Omega}(E, L, N)$ denote the number of micro states of the (macroscopic) system with energy less than or equal to E.

(i) Show that[5],

$$\widehat{\Omega}(E, L, N) = \frac{1}{h^N} \frac{L^N}{N!} \frac{(2\pi m E)^{N/2}}{\Gamma\left(\frac{N}{2}+1\right)}$$

(ii) Derive an expression for the density of states of a single particle.

Carry out quantum-counting of micro states of a single particle confined to a one dimensional segment of length L and

(iii) show that the resulting expression is the same as the one obtained by classical Boltzmann counting.

2.5 A macroscopic system can be in any one of the two energy levels labelled **1** and **2**, with probabilities p_1 and p_2 respectively. The degeneracy of the energy level labelled **1** is g_1 and that of the energy level labelled 2 is g_2. Show that entropy of the system is given by,

$$S = -k_B \sum_{i=1}^{2} p_i \ln p_i + \sum_{i=1}^{2} p_i [k_B \ln g_i]$$

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[4]Hint : The microstate of a single particle in two dimension, is specified a string of four numbers, two for position and two for momentum. The microstate of N particles is specified by an ordered string of $4N$ numbers.

[5]Hint : The micro state of a single particle in one dimension is specified by two numbers, one for position and one for momentum. The micro state of N particles in one dimension requires an ordered string of $2N$ numbers.

PROBLEM SET - 3
23 January 2017

3.1 Consider an isolated system of N non-interacting particles occupying two states of energies $-\epsilon$ and $+\epsilon$. The energy of the system is E. Let $x = \dfrac{E}{N\epsilon}$.

   (i) Show that the entropy of the system is given by[6]

$$S(E) = Nk_B \left[\left(\frac{1+x}{2} \right) \ln \left(\frac{2}{1+x} \right) + \left(\frac{1-x}{2} \right) \ln \left(\frac{2}{1-x} \right) \right]$$

   (ii) Show that $\beta = \dfrac{1}{k_B T} = \dfrac{1}{2\epsilon} \ln \left(\dfrac{1-x}{1+x} \right)$

3.2 A particular system obeys the fundamental equation,

$$U = A \, \frac{N^3}{V^2} \exp \left(\frac{S}{Nk_B} \right),$$

where A (joule metre^2) is a constant. Initially the system is at $T = 317.48$ kelvin, and $P = 2 \times 10^5$ pascals. The system expands reversibly until the pressure drops to a value of 10^5 pascals, by a process in which the entropy does not change. What is the final temperature[7] ?

3.3 Roll two independent fair dice. Let n_1 and n_2 denote the results of the first and the second die respectively. Define a random variable as follows.

$$n = \begin{cases} max(n_1, n_2) & \text{if } n_1 \neq n_2 \\[2mm] n_1 & \text{if } n_1 = n_2 \end{cases}$$

Find the mean and variance of n.

3.4 Let $x = X(\omega)$ denote a real random variable and $f(x)$ its probability density function. The characteristic function of the random variable is given by the Fourier transform of

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[6]HINT : Let n_1 and n_2 denote the number of particles in the two states of energy $-\epsilon$ and $+\epsilon$ respectively. We have $\widetilde{\Omega} = N!/(n_1! n_2!)$; $S = k_B \ln \widetilde{\Omega}$; Calculate n_1 and n_2 by solving : $n_1 + n_2 = N$ and $n_2 \epsilon - n_1 \epsilon = E$.

[7]HINT: Take partial derivatives of U with respect to S and V and get T and P respectively. Find a relation between P and T when entropy does not change.

its density function :

$$\phi(k) = \int_{-\infty}^{+\infty} dx \ \exp(-ikx) f(x) \ = \ \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \int_{-\infty}^{+\infty} dx \ x^n \ f(x)$$

$$= \ \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} M_n$$

where M_n denotes the n-th moment. The coefficient of $(-ik)^n/n!$ in the power series expansion of the characteristic function gives the n-th moment.

Consider random variable x with an exponential probability density function,

$$f(x) \ = \ \exp(-x) \text{ for } 0 \le x \le +\infty$$

- Show that the characteristic function of the exponential random variable is given by,

$$\phi(k) \ = \ \frac{1}{1 + ik}$$

- From the characteristic function derive expressions for the moments of the exponential random variable and show that

$$M_n = \langle x^n \rangle = \int_0^{\infty} dx \ x^n \ \exp(-x) = \Gamma(n+1) = n!$$

3.5 Take a p-coin[8]. Toss the coin independently until "Heads" appears for the first time whence the game stops.

- What are the elements of the sample space ?

Let n denote the number of "Tails" in a game.

- Derive an expression for $P(n)$ - the probability distribution function of the integer random variable n.

The moment generating function is defined as $\widetilde{P}(z) = \sum_{n=0}^{\infty} z^n \ P(n)$.

- Show that the the moment generating function of the random variable n is given by

$$\widetilde{P}(z) = \frac{p}{1 - qz}.$$

- From the moment generating function calculate the mean, ζ, and variance σ^2 of the random variable n.
- Show that $P(n)$ and $\widetilde{P}(z)$ can be expressed as,

$$P(n) \ = \ \frac{\zeta^n}{(1 + \zeta)^{n+1}}$$

$$\widetilde{P}(z) \ = \ \frac{1}{1 + \zeta(1 - z)}$$

[8]A p-coin is one for which the probability of "Heads" is p and that of "Tails" is $q = 1 - p$.

PROBLEM SET - 4 30 January 2017

4.1 A closed system consists of $3N$ classical non-interacting an-harmonic oscillators in equilibrium at temperature T. The energy of a single an-harmonic oscillator is given by

$$E(q, p) \; = \; \frac{p^2}{2m} + bq^{2\nu} \;\; \text{where } \nu \; \geq \; 2 \text{ is an integer and } b \text{ is a constant.}$$

  (i) Derive an expression for the canonical partition function by carrying out the following integral :

$$Q \; = \; \frac{1}{h} \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} dp \; \exp\left[-\beta \left(\frac{p^2}{2m} + bq^{2\nu} \right) \right]$$

  (ii) Show that the heat capacity of the system is given by[9]

$$C = \frac{\partial \langle E \rangle}{\partial T} = \left(\frac{\nu + 1}{2\nu} \right) 3Nk_B.$$

4.2 Consider a system of N distinguishable non-interacting particles each of which can be in states designated as **1** and **2**. Energy of state **1** is $\epsilon_1 = -\epsilon$ and that of state **2** is $\epsilon_2 = +\epsilon$. Let the number of particles in states **1** and **2** be N_1 and N_2 respectively. We have

$$N = N_1 + N_2$$

and

$$E = N_1 \epsilon_1 + N_2 \epsilon_2 = (2N_2 - N)\epsilon.$$

  (i) Evaluate canonical partition function $Q(T, V, N)$. Do not forget the degeneracy factor, $\widehat{\Omega}$ which gives the number of ways we can organize N_1 particles in state **1** and N_2 particles in state **2**.

  (ii) Let $q(T, V)$ be the single-particle partition function. How $Q(T, V, N)$ and $q(t, V)$ are related ?

  (iii) Calculate and sketch heat capacity C_V of the system.

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[9]When $\nu = 1$ and $b = (1/2)m\omega^2$, we recover the results for simple harmonic oscillators : $C = 3Nk_B$. This corresponds to the heat capacity of a crystalline solid having N atoms/molecules organized in a lattice. We have $C = 3Nk_B = 3nR$ or molar specific heat is $c = 3R = 5.958 \approx 6$ Calories $\Rightarrow$ Dulong-Petit's law.

Practice Problems : Lagrange Method of undetermined multiplier

4.3 Maximise $A(x_1, x_2) = x_1 x_2$ under constraint $x_1 + x_2 = 10$.

4.4 Maximise $f(x, y) = x^3 y^5$ under the constraint $x + y = 8$. (Answer: $x = 3; y = 5$.)

4.5 Let (x, y, x) be a point on the surface of a sphere $x^2 + y^2 + z^2 = 1$. Let $P = (2, 1, -2)$ be a point. Let $D(x, y, z)$ denote the distance between the point (x, y, z) on the sphere and P. Employing Lagrange's method of undetermined multiplier, find the maximum and minimum value of D. (Answer: 4 and 2)

4.6 A rectangle is inscribed in an ellipse whose major and minor axes are of lengths a and b respectively. The major axis is along the X axis and the minor axis is along the Y axis. The centre of the ellipse is at the origin. The centre of the inscribed rectangle is also at origin. Find the length and breath of the rectangle with largest possible area. Employ the method of Lagrange multiplier. If you have a circle of radius R with centre at origin instead of ellipse what would be the length and breath of the inscribed rectangle with largest possible area ?

4.7 Consider a right circular cylinder of volume 2π cubic meter. Employing the method of Lagrange multiplier find out what height and radius will provide the minimum total surface area for the cylinder ?

4.8 Consider the distribution

$$\widehat{\Omega}(n_1, n_2, n_3, n_4, n_5, n_6) = \frac{N!}{\prod_{i=1}^{6} n_i \, !}$$

where n_1 is the number of "ones", n_2 is the number of "Twos" *etc.* in a toss of N independent fair dice. Let $n_i^\star$ denote the value of n_i, for which $\widehat{\Omega}(n_1, n_2, \cdots, n_6)$ is maximum under the constraint

$$\sum_{i=1}^{6} n_i = N \ .$$

(i) Employing Lagrange's method of undetermined multiplier, find $n_i^\star \ : \ i = 1, 2, \cdots, 6$.

(ii) Let $\langle n_i \rangle$ denote the average of n_i. Show that $n_i^\star = \langle n_i \rangle \ : i = 1, 2, \cdots, 6$.

4.9 Boltzmann -Gibbs-Shannon entropy is given by

$$S(p_1, p_2, \cdots) = -k_B \sum_i p_i \ln p_i,$$

where p_i is the probability of the micro state (indexed by i) of a closed system. Employing the method of Lagrange undetermined multiplier,

(i) find $\{p_i \ : \ i = 1, 2, \cdots\}$ for an isolated system by maximising the entropy under a single constraint : $\sum_i p_i = 1$

(ii) find $\{p_i \ : \ i = 1, 2, \cdots\}$ for a closed system by maximising the entropy under two constraints

(a) $\sum_i p_i = 1$ and

(b) $\sum_i p_i \epsilon_i = U$ where U is the thermodynamic internal energy.

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PROBLEM SET - 5   6 February 2017

5.1 Consider a system of two non-interacting particles in thermal equilibrium at temperature $T = 1/[k_B \beta]$. Each of the particles can occupy any of the three quantum states. The energies of the quantum states are : $-\epsilon, \quad 0 \quad \text{and} \quad +\epsilon.$ Obtain canonical partition function of the system for particles obeying

   (i) classical statistics[10] and are distinguishable

   (ii) Maxwell-Boltzmann statistics[11] and are 'indistinguishable ' .

   For each of the above two cases calculate average energy of the system.

5.2 A zipper has N links. Each link can be in any one of the two states

   (a) a closed state with zero energy

   (b) an open state with energy $\epsilon > 0$.

   The zipper can be unzipped from top to bottom. A link can be open if and only if all the links above it are also open. In other words, if we number the links as $1, \ 2, \ \cdots, \ N$ from top to bottom, then link k can be open if and only if all the links from 1 to $k-1$ are also open.

   (i) Derive an expression for the canonical partition function

   (ii) Let n denote the number of open links. Derive an expression for the average number, $\langle n \rangle$ of open links. Employ canonical ensemble for carrying out the averaging process.

   (iii) Show that at low temperatures $(k_B T \ << \ 1)$, the average $\langle n \rangle$ is independent of N.

5.3 The expression for the average energy in statistical mechanics which corresponds to thermodynamic internal energy is given by

$$\langle E \rangle = U \ = \ -\frac{\partial \ln \ Q}{\partial \beta}$$

Show that for an ideal gas the energy is given by

$$\langle E \rangle = U \ = \ 3N\frac{k_B T}{2}$$

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[10]do not divide by $N!$

[11]divide by $N!$

consistent with equi-partition theorem which says that each degree of freedom (each quadratic term in the Hamiltonian) carries an energy of $k_B T/2$.

5.4 Consider a closed system of $3N$ non-interacting, identical, distinguishable, quantum oscillators. The system is in thermal equilibrium at temperature T.

Consider three cases :

- **Case - 1** :

  the energy levels of a single oscillator is given by

  $$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \; ; \quad n = 0, 1, 2, \cdots .$$

  (i) Derive an expression for the canonical partition function.
  (ii) derive an expression for the internal energy $U(T)$
  (iii) Obtain $U(T)$ in the classical limit : $k_B T \gg \hbar\omega$. Show that we recover the results of classical harmonic oscillator : $U = Nk_B T$, $C_V = Nk_B$.
  (iv) Derive an expression for entropy; obtain entropy in the classical limit

- **Case - 2** : "Even-harmonic oscillators" :

  the energy levels of the oscillator are given by

  $$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \; ; \quad n = 0, 2, 4, \cdots .$$

  Note n is zero or an even number.

  (i) Derive an expression for the canonical partition function.
  (ii) derive an expression for the internal energy $U(T)$
  (iii) Obtain $U(T)$ in the classical limit : $k_B T \gg \hbar\omega$. Show that we recover the results of classical harmonic oscillator : $U = Nk_B T$, $C_V = Nk_B$.
  (iv) Derive an expression for entropy. Obtain S in the classical limit and show the results are consistent what you have obtained in case-1.

- **Case - 3** : "Odd-harmonic oscillators" :

  the energy levels of the oscillator are given by

  $$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0 \; ; \quad n = 1, 3, 5, \cdots .$$

  Note n is an odd number.

  (i) Derive an expression for the canonical partition function.
  (ii) derive an expression for the internal energy $U(T)$
  (iii) Obtain $U(T)$ in the classical limit : $k_B T \gg \hbar\omega$. Show that we recover the results of classical harmonic oscillator : $U = Nk_B T$, $C_V = Nk_B$.
  (iv) Derive an expression for entropy. Obtain S in the classical limit and show the results are consistent what you have obtained in case-1.

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PROBLEM SET - 6

13 February 2017

6.1 We saw that the parameter $\boldsymbol{\rho \Lambda^3}$ helps us to find when quantum effects come into play toward determining the properties of an ideal gas. We have,

$$\boldsymbol{\rho \;=\; \frac{N}{V}}; \qquad \boldsymbol{\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}}$$

$\boldsymbol{\rho}$ is the number density and $\boldsymbol{\Lambda}$ is the thermal / quantum wave length[12].

$\boldsymbol{\rho^{-1} = N/V}$ is the effective volume available per molecule. Therefore $\boldsymbol{\rho^{-1/3}}$ is a measure of the average distance between two molecules. $\boldsymbol{\Lambda}$ is a measure of the de Broglie wavelength associated with a particle having energy $\boldsymbol{k_B T}$. If $\boldsymbol{\rho^{-1} >> \Lambda^3}$, we can ignore quantum effects. This is equivalent to saying that if $\boldsymbol{\rho \Lambda^3 \; << \; 1}$ we can ignore quantum effects. When $\boldsymbol{\rho \Lambda^3 \; >> \; 1}$ quantum effects come into play. Set $\boldsymbol{\rho \Lambda^3 \; = \; 1}$ and derive an expression for the temperature. Let $\boldsymbol{T = T^\star}$ denote the temperature. Calculate the value of $\boldsymbol{T^\star}$ for the following cases : 1. Hydrogen gas, 2. liquid Helium, and 3 electrons in metals.

DATA

System	density $\boldsymbol{\rho}$	mass $\boldsymbol{m}$
Hydrogen	$\boldsymbol{2 \times 10^{25}}$ per cubic meter	1.008 amu
Liquid Helium	$\boldsymbol{2 \times 10^{28}}$ per cubic meter	4.003 amu
electrons in metal	$\boldsymbol{10^{28}}$ per cubic meter	$\boldsymbol{9.109 \times 10^{-31}}$ kg.

h	$\boldsymbol{6.626 \times 10^{-34}}$ joule sec.
$k_{\boldsymbol{B}}$	$\boldsymbol{1.389 \times 10^{-23}}$ joules per kelvin
1 amu	$\boldsymbol{1.661 \times 10^{-27}}$ kg.

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[12]check $\boldsymbol{\Lambda}$ has the dimension of length.

6.2 See S. B. Cahn, G. D. Mahan, and B. E. Nadgorny,
A Guide to Physics Problems Part 2: Thermodynamics, Statistical Physics, and Quantum Mechanics,
Plenum ((1997) problem No. 4.45 page 24

Consider a system composed of a very large number N of distinguishable particles at rest. The particles do not interact with each other. Each particle has only two non-degenerate energy levels: 0 and $\epsilon > 0$. Let E denote the total energy of the system. Note that E is a random variable; it varies, in general, from one micro state of the system to the other. Let $\xi = E/N$ denote energy per particle.

(a) Assume that the system is not necessarily in thermal equilibrium. What is the maximum possible value of ξ ?

(b) Let the system be in thermal equilibrium at temperature T. The canonical ensemble average of E is the the thermodynamic energy, denoted by U. *i.e.* $U = \langle E \rangle$, where $\langle \cdot \rangle$ denote an average over a canonical ensemble[13]. Let $\zeta = U/N$ denote the (thermodynamic, equilibrium) energy per particle. Derive an expression for ζ as a function of temperature.

(c) Find the value of ζ in the limit $T \to 0$ and in the limit $T \to \infty$.

(d) What is the maximum possible value that ζ can take ?

6.3 A closed system having three non-degenerate levels of energies $-\epsilon_0$, 0, and $+\epsilon_0$ is at temperature T.

(i) Let $\beta\epsilon_0 = 2$. The probability of finding the system in the level of energy 0 is

(a) $\dfrac{1}{2} \cosh 2$ (b) $\dfrac{1}{\cosh 2}$

(c) $\dfrac{1}{2 \cosh 2}$ (d) $\dfrac{1}{1 + 2 \cosh 2}$

(ii) Let $\beta\epsilon_0 = x$. In the limit $T \to \infty$, the (Helmholtz) free energy of the system is

(a) $-Nk_BTx^2$ (b) $-Nk_BT \left[\ln 2 + \dfrac{x^2}{2} \right]$

(c) $-Nk_BT \left[\ln 3 + \dfrac{x^2}{3} \right]$ (d) $-Nk_BT \ln 3$

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[13]Note that it is meaningful to call U as thermodynamic energy only when the average of energy is calculated for $N \to \infty$; only in this limit the average energy will be unchanging with time. Fluctuations around the average value, defined as the standard deviation (*i.e.* square-root of the variance) of energy divided by the mean energy will be of the order of $1/\sqrt{N}$; this goes to zero only in the limit of $N \to \infty$.

STATISTICAL MECHANICS $\qquad$ K P N and A K K

PROBLEM SET - 7 $\qquad$ 6 March 2017

7.1 A thermodynamic system obeys the following fundamental equation,

$$S \; = \; Nk_B \ln\left[\frac{1}{v_0 k_B T_0}\frac{UV}{N^2}\right]$$

where k_B, v_0, T_0 are constants.

(i) Derive an expression for the micro canonical temperature $T(U, V, N)$, and pressure[14] $P(U, V, N)$.

(ii) Derive an expression for Helmholtz free energy[15] $F(T, V, N)$

(iii) Derive an expression for Gibbs free energy[16].

7.2 A system has

(i) a non-degenerate ground state of zero energy

(ii) a non-degenerate excited state of energy $100k_B$ joules

(iii) a doubly-degenerate excited state of energy $300k_B$ joules

The Boltzmann constant k_B equals 1.3807×10^{-23}.

Calculate the relative fluctuations of energy given by $\eta = \sigma_E/\langle E\rangle$, at $= 200$ kelvin. Note : $\sigma_E^2 = \langle E^2\rangle - \langle E\rangle^2$. The angular brackets denote averaging over a canonical ensemble. Some useful relations :

$$\langle E\rangle \; = \; -\frac{1}{Q}\frac{\partial Q}{\partial \beta} \quad \text{and} \quad \langle E^2\rangle = \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2} \quad \text{or} \quad \sigma_E^2 = \frac{\partial}{\partial \beta}\left[\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right]$$

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[14] $\left(\dfrac{\partial S}{\partial U}\right)_{V,N} = \dfrac{1}{T}; \quad \left(\dfrac{\partial S}{\partial V}\right)_{U,N} = \dfrac{P}{T}$

[15] Express U as a function of S, V, and N. Carry out Legendre transform : $S \to T$ and $U \to F$. (i) Take the partial derivative of U with respect to S and get T as a function of S, V, and N. (ii) Invert and get S as a function of T, V, and N. Also get U as a function of T, V, and N. (iii) $F = U - TS$, wherein eliminate U, and S in favour of T, V and N.

[16] Legendre transform : $S \to T$, $V \to P$ and $U \to G$. $G(T, P, N) = U - TS + PV$

7.3 R K Pathria, *Statistical Mechanics*, Second Edition, Butterworth and Henemann (1996) page 102, Problem 4.4

Show that the probability that an open system has N particles is given by

$$P(N) = \frac{\exp(\beta\mu N)Q(T, V, N)}{\mathcal{Q}(T, V, \mu)}$$

For a classical indistinguishable ideal gas, show that $P(N)$ is a Poisson distribution. Let σ_N^2 denote the variance N. Show that,

$$\sigma_N^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}$$

where $\langle N \rangle$ is the average number of particles in the open system : averaging is carried out over a grand canonical ensemble.

7.4 Avjit Lahiri, *Statistical Mechanics : An Elementary Outline*, Revised Edition, Universities Press (2008)p.136;Problems 3-4

A system has two energy levels, one of zero energy and degeneracy g_0. and the other of ϵ energy and degeneracy g_1. Show that

(i) the entropy of the system is given by

$$S = \frac{g_1 \epsilon \exp(-\beta\epsilon)}{T[g_0 + g_1 \exp(-\beta\epsilon)]} + k_B \ln[g_0 + g_1 \exp(-\beta\epsilon)]$$

(ii) the heat capacity is given by, $C = \dfrac{g_0 g_1 \epsilon^2 \exp(-\beta\epsilon)}{k_B T^2 [g_0 + g_1 \exp(-\beta\epsilon)]^2}$.

(iii) at low temperatures, $C \sim T^{-2} \exp(-\epsilon/[k_B T])$

(iv) at high temperatures $C \sim T^{-2}$.

7.5 Donald McQuarrie, *Statistical Mechanics*, Harper and Row (1976)page 65, Problem 3-4

Consider an open system described by a grand canonical ensemble. Show that the pressure of an open system is given by

$$P = k_B T \left(\frac{\partial \ln \mathcal{Q}}{\partial V}\right)_{\mu,V}.$$

Euler Theorem : If $f(x, y)$ is a homogeneous function of first order, then

$$f(x, y) = x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y}.$$

Employ Euler theorem and show that

$$P = \frac{k_B T}{V} \ln \mathcal{Q}(T, V, \mu)$$

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STATISTICAL MECHANICS   K P N and A K K

PROBLEM SET - 8   13 March 2017

8.1 We have,

$$-\frac{S}{k_B} = \sum_i p_i \, \ln(p_i).$$

The micro states are labelled by $\{i : i = 1, 2, \cdots\}$ and $\{p_i : i = 1, 2, \cdots\}$ are the corresponding probabilities. In the above the right hand side can be interpreted as $\langle \ln(p) \rangle$. Consider a closed system for which

$$p_i = \frac{1}{Q} \exp(-\beta \epsilon_i),$$

where $\{\epsilon_i : i = 1, 2, \cdots\}$ are the energies of the microstates and

$$Q = \sum_i \exp(-\beta \epsilon_i)$$

is the canonical partition function. Show that

$$-\frac{S}{k_B} = -\beta U - \ln Q,$$

where $U = \langle E \rangle = \sum_i p_i \epsilon_i$. From the above deduce that $F = -k_B T \ln Q$.

8.2 R. K Pathria, *Statistical Mechanics*, Second Edition, Butterworth-Heinemann (1996) page : 85; Problem : 3.18

Show that for a closed system described by a canonical ensemble,

$$\langle (E - \langle E \rangle)^3 = k_B^2 \left[T^4 \left(\frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right].$$

Verify the following relation for ideal gas.

$$\frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle^2} = \frac{2}{3N}$$

$$\frac{\langle (E - \langle E \rangle)^3 \rangle}{\langle E \rangle^3} = \frac{8}{9N^2}$$

8.3 Let $\langle N \rangle$ denote the average number of particles in an open system. Show that

$$\langle N \rangle = \lambda \, \frac{1}{\mathcal{Q}(T, V, \mu)} \frac{\partial \mathcal{Q}}{\partial \lambda},$$

In the above λ is the fugacity. $\lambda = \exp(\beta\mu)$, where μ is the chemical potential[17] : energy change per addition of a particle at constant entropy and volume. $\mathcal{Q}(T, V, \mu)$ is the grand canonical partition function.

8.4 Let $P(N)$ denote the probability that there are N particles in an open system at temperature T and chemical potential μ. Show that

$$P(N) = \frac{\zeta^N \exp(-\zeta)}{N!},$$

where

$$\zeta = \langle N \rangle = \sum_{N=0}^{\infty} N \, P(N).$$

8.5 Donald A McQuarrie, *Statistical Mechanics*, Harper and Row (1976) page : 67; Problem : 3-22.

Show that the fluctuations of energy in a grand canonical ensemble is

$$\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial \langle E \rangle}{\partial \langle N \rangle} \right)_{T,V} \sigma_N^2$$

8.6 Start with Helmholtz free energy $F(T, V, N)$. We have

$$F(T, \lambda V, \lambda N) = \lambda F(T, V, N).$$

Show that Euler's theorem implies that $F = \mu N - PV$. From these considerations derive Gibbs-Duhem relation,

$$d\mu = vdP - sdT,$$

where $v = V/N$ is the specific volume and $s = S/N$ is the specific entropy.

8.7 Starting with Gibbs' free energy $G(T, P, N)$ and the fact that G is a first order homogeneous function of N, derive Gibbs'-Duhem relation.

8.8 Employing the grand canonical ensemble formalism, show that the fluctuations in the number of particles, $\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2$, in an open system is related to the isothermal compressibility κ_T, as given below.

$$\sigma_N^2 = \frac{\langle N \rangle^2 k_B T}{V} \kappa_T,$$

where,

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

---

[17] $\mu = \left(\dfrac{\partial U}{\partial N} \right)_{S,V}$ or $\mu = -T \left(\dfrac{\partial S}{\partial N} \right)_{U,V}$

PROBLEM SET - 9
<div align="right">20 March 2017</div>

9.1 Consider a closed system of **THREE** non-interacting particles at temperature T occupying

- a non-degenerate ground state of energy zero and
- a three-fold degenerate excited state of energy ϵ.

■ Derive expressions for the canonical partition function when the particles obey,

(i) classical statistics - particles are distinguishable[18]

(ii) Maxwell Boltzmann statistics - particles are indistinguishable[19]

(iii) Bose-Einstein statistics, and

(iv) Fermi-Dirac statistics.

HINT : Explicitly enumerate all possible strings of occupation numbers

$$\{n_1, n_2, n_3, n_4\}$$

for the four quantum states

$$\{1, 2, 3, 4\}$$

with energies

$$\{\epsilon_1 = 0, \epsilon_2 = \epsilon, \epsilon_3 = \epsilon, \epsilon_4 = \epsilon\}$$

with the constraint

$$n_1 + n_2 + n_3 + n_4 = 3$$

. Keep track of the degeneracy factor Ω - the 'number' of micro states for each string.

$\Omega = 1$ for Bose-Einstein and Fermi-Dirac statistics;

$\Omega = \dfrac{3!}{\prod_{i=1}^{4} n_i!}$ for classical statistics and

$\Omega = \dfrac{1}{\prod_{i=1}^{4} n_i!}$ (which is not an integer for several strings!) for Maxwell-Boltzmann statistics.

■ For each statistics, calculate the average energy.

---

[18]do not divide by $N!$

[19]in the sense meant by Boltzmann. Divide by $N!$ - as suggested by Boltzmann, to correct for the over counting of micro states. This is called Boltzmann counting.

9.2 R. K. Pathria, *Statistical Mechanics*, Second Edition, Butterworth-Heinemann (1996) Page : 152; Problem : 6.1; Donald A McQuarrie, *Statistical Mechanics* Harper and Row (1976) Page : 78; Problem : 4-8

Show that the entropy of ideal quantum particles can be expressed as

$$
S = \begin{cases} -k_B \sum_i \left[\langle n_i \rangle \ln \langle n_i \rangle + (1 + \langle n_i \rangle) \ln(1 + \langle n_i \rangle) \right] & \text{for bosons} \\[2ex] -k_B \sum_i \left[\langle n_i \rangle \ln \langle n_i \rangle + (1 - \langle n_i \rangle) \ln(1 - \langle n_i \rangle) \right] & \text{for fermions} \end{cases}
$$

HINT : Let $p_{i,n}$ denote the probability that the i th quantum state holds n particles. The entropy is given by

$$
S = -k_B \sum_i \sum_n p_{i,n} \ln(p_{i,n}).
$$

The distribution $p_{i,n}$ for a given i is

> binomial for fermions and
>
> geometric for bosons.

These are single parameter distributions with the parameter given by $\zeta_i = \langle n_i \rangle = \sum_n n p_{i,n}$.

9.3 Consider an open system of non-interacting particles occupying single particle quantum states labelled by $i = 1, 2, \cdots$. Let $P(n)$ denote the probability that there are n particles in quantum state k. The probability that there is no particle in state k is given to be **0.001**; in other words, $P(n = 0) = 0.001$ What is the average number of particles in the state k if the particles obey

   (i) Maxwell-Boltzmann statistics,
   (ii) Bose-Einstein statistics,
   (iii) Fermi-Dirac statistics.

HINT : Consider the distribution of n under the three statistics. It is Poisson for Maxwell-Boltzmann statistics; geometric for bosons; and binomial for fermions. Each is a single parameter distribution. You can conveniently take that parameter as $\zeta = \langle n_k \rangle$. Evaluate ζ employing the data given namely $P(n = 0) = 0.001$

9.4 Show that the grand canonical partition function for Fermions is given by

$$
\mathcal{Q}(T, V, \mu) = \prod_i \left[1 + \exp\left\{ -\beta \left(\epsilon_i - \mu \right) \right\} \right]
$$

Let $f(\epsilon_i) = \langle n_i \rangle$, where n_i is the number of Fermions in quantum state i. The energy of the quantum state i is ϵ_i. The angular bracket denotes an average over a grand canonical ensemble of micro states. Consider energy to be a continuous variable and denote it by ϵ. Show that

$$
f(\epsilon) = \frac{1}{\exp\left[\beta \left(\epsilon - \mu \right) \right] + 1}
$$

   (i) Sketch the function the Fermi function f at zero temperature.
   (ii) Show that the Fermi function has the following symmetry :

$$
f(\epsilon = \mu + \xi) = 1 - f(\epsilon = \mu - \xi).
$$

STATISTICAL MECHANICS K P N and A K K

PROBLEM SET - 10 27 March 2017

10.1 Show analytically

$$
I_1 = \sum_{N=0}^{\infty} \sum_{\{n_1, n_2\}}^{\star} x_1^{n_1} x_2^{n_2} = \left(\frac{1}{1 - x_1} \right) \left(\frac{1}{1 - x_2} \right)
$$

where the superscript $\star$ indicates the restriction

$$
n_1 + n_2 = N.
$$

Thus $I_1 = I_2$ where,

$$
I_2 = \left(\sum_{n=0}^{\infty} x_1^n \right) \times \left(\sum_{n=0}^{\infty} x_2^n \right) = \left(\frac{1}{1 - x_1} \right) \left(\frac{1}{1 - x_2} \right)
$$

HINT :

$$
\sum_{N=0}^{\infty} \sum_{\{n_1, n_1\}}^{\star} x_1^{n_1} x_2^{n_2} = \sum_{N=0}^{\infty} \sum_{n=0}^{N} x_1^n x_2^{N-n} = \sum_{N=0}^{\infty} \frac{x_2^{N+1} - x_1^{N+1}}{x_2 - x_1} = \cdots
$$

10.2 Let the number of single-particle quantum states be four; these are labelled

1, 2, 3, 4.

Three non interacting quantum particles occupy these states. Let

$$(n_1, \ n_2, \ n_3, \ n_4)$$

denote a string of occupancy numbers of the four quantum states. Note the constraint

$$
\sum_{i=1}^{4} n_i = 3.
$$

Each string corresponds to a micro state of the three particle system. What are the micro states if the particles are 1. bosons and 2. fermions. (Hint : there are four micro states for fermions and twenty for bosons.). How many micro states are there for classical distinguishable particles and how do you represent them ? How many micro states are there for particles obeying Maxwell-Boltzmann statistics : and is your answer a whole number ?

10.3 E Atlee Jackson, *Equilibrium Statistical Mechanics*, Prentice Hall (1968) p.111; Problem.2

A simple system has five micro states with energies

$$-1, \ 0, \ 0, \ 0, \ +1 \ \times \ 10^{-20} \ \text{joules.}$$

(a) Determine the probability that the system is in these different micro states when it is at temperatures $T = 200$ kelvin, 400 kelvin.

(b) In each case what is the probability that the energy of the system is zero ?

(c) What is the relative chance of finding the system in a state with $E = -1 \times 10^{-20}$ joules compared to the chance of finding the system in a state with $E = +1 \times 10^{-20}$ joules ?

(d) Set up a general expression for the relative probability of finding the system in a state with $E = E_1$ and with $E = E_2$ in terms of β and the canonical partition function Q.

10.4 E Atlee Jackson, *Equilibrium Statistical Mechanics*, Prentice Hall (1968) p.112; Problem.4

System-1 has micro states of energies

$$\{\epsilon_k \ : \ k = 1, 2, \cdots \}.$$

Its internal energy is denoted by the symbol U. Consider system-2 with micro states with energies

$$\epsilon'_k = \epsilon_k + \epsilon,$$

where ϵ is a constant. Let U' be the internal energy of system-2. Find the relation between U and U'. What is the physical significance of the change in the internal energy.

10.5 Show that for bosons

$$\rho \Lambda^3 = \frac{\Lambda^3}{V} \frac{\lambda}{1 - \lambda} + g_{3/2}(\lambda) \tag{1}$$

where the number density $\rho = N/V$, the thermal wavelength

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}},$$

$\lambda = \exp(\beta \mu)$ is the fugacity (μ is chemical potential), and

$$g_{3/3}(\lambda) = \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}}.$$

Show that for particles obeying Maxwell-Boltzmann statistics

$$\rho \Lambda^3 = \lambda. \tag{2}$$

Show that in the classical limit of $\rho \Lambda^3 \to 0$ the equation (??) for bosons reduces to the equation (??) for particles obeying Maxwell-Boltzmann statistics.