Indian Institute of Technology Bhubaneswar
School of Basic Sciences

Spring Mid-Semester Examination-2017

Subject Name : Statistical Mechanics	**Subject Code : PH5L008**

Date : 21 February 2017

Duration : 2 Hours   **Full Marks : 30**

> Answer a new question on a fresh page (strictly) and all parts of a question together

Question - 1

The canonical partition function of some kind of particles is given by,

$$Q(\beta, V, N) = \left(\frac{V - Nb}{\Lambda^3}\right)^N \exp\left(\frac{aN^2}{k_B T V}\right),$$

where,

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

is the thermal wavelength or quantum wavelength. a, and b are constants; other symbols have their usual meaning.

(i) Find the internal energy $U(T, V, N)$.   **(2 Marks)**

(ii) Find the entropy, $S(T, V, N)$.   **(2 Marks)**

(iv) Does the expression for S, provide a valid fundamental relation[1]? If not, what is wrong with S ? How can Q be corrected ?   **(2 Marks)**

                                                    (Total : 6 Marks)

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[1]except perhaps at $T = 0$.

SOLUTION

(i) **ENERGY**

$$\ln Q = N \ln \left(\frac{V - Nb}{\Lambda^3} \right) + \frac{\beta a N^2}{V}$$

$$\frac{\partial \ln Q}{\partial \beta} = -\frac{3N}{\Lambda} \frac{\partial \Lambda}{\partial \beta} + \frac{a N^2}{V}$$

$$= -3N \frac{\partial \ln \Lambda}{\partial \beta} + \frac{a N^2}{V}$$

We have,

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{2\pi m}} \beta^{1/2}$$

$$\ln \Lambda = \frac{1}{2} \ln \beta + \ln \left(\frac{h}{\sqrt{2\pi m}} \right)$$

$$\frac{\partial \ln \Lambda}{\partial \beta} = \frac{1}{2\beta} = \frac{k_B T}{2}$$

Therefore,

$$\frac{\partial \ln Q}{\partial \beta} = -\frac{3N}{2} k_B T + \frac{a N^2}{V}$$

$$E = -\frac{\partial \ln Q}{\partial \beta} = \frac{3N k_B T}{2} - \frac{a N^2}{V}$$

(ii) **ENTROPY**
Let us first calculate the free energy,

$$F = -k_B T \ln Q$$

$$= -N k_B T \ln \left(\frac{V - Nb}{\Lambda^3} \right) - \frac{a N^2}{V}$$

Entropy is given by,

$$S = \frac{U - F}{T}$$

$$= \frac{3 N k_B}{2} + N k_B \ln \left(\frac{V - Nb}{\Lambda^3} \right)$$

(iii) **ISSUES ON THE EXPRESSION FOR ENTROPY**
Note at $T = 0$, we find $E = F = -aN^2/V$ and hence $S = 0$ which is consistent with thermodynamics. However for $T \neq 0$, the expression for entropy does not

provide a valid fundamental equation because it is not extensive. In other words $S(T, \eta V, \eta N) \neq \eta S(T, V, N)$. Note T is intensive. S has to be first order homogeneous function of its extensive variables only.

To render entropy extensive, Boltzmann introduced the notion of indistinguishability of particles; swapping of particles does not produce a new micro state. There are $N!$ micro states that can be produced by particle swapping. Boltzmann recommended division by $N!$. We can correct the canonical partition function by introducing Boltzmann counting, and we get,

$$Q(\beta, V, N) = \frac{1}{N!} \left(\frac{V - Nb}{\Lambda^3} \right)^N \exp \left(\frac{aN^2}{k_B T V} \right),$$

We have,

$$\ln Q = N \ln \left(\frac{V - Nb}{N\Lambda^3} \right)^N + \frac{\beta a N^2}{V} + N$$

It is clear from the above that the expression for energy[2] will be the same as earlier. The free energy is given by,

$$F = -Nk_B T \ln \left(\frac{V - Nb}{N\Lambda^3} \right) - \frac{aN^2}{V} - Nk_B T$$
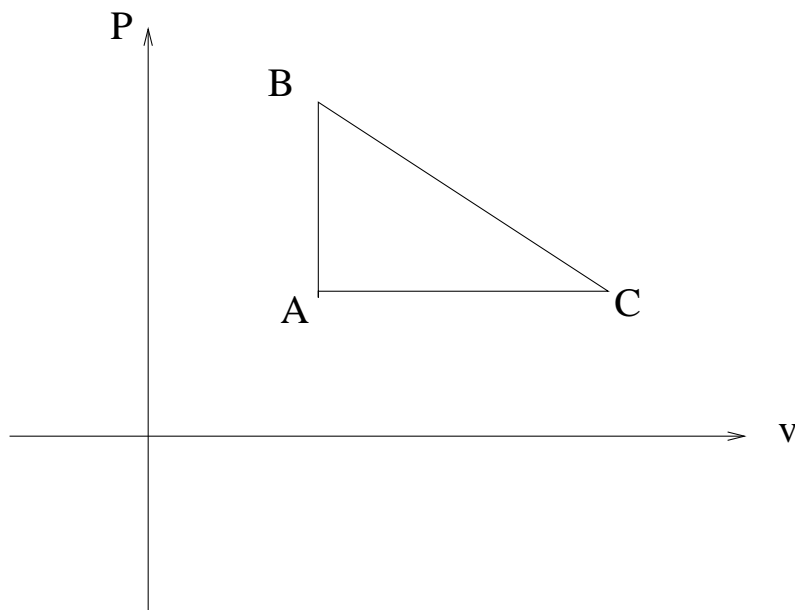
Entropy

$$S = \frac{5Nk_B}{2} + Nk_B \ln \left(\frac{V - Nb}{N\Lambda^3} \right)$$

The above expression for entropy is extensive and hence consistent with thermodynamics.

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[2]Energy obtained by taking partial derivative of $\ln Q$ with respect to β

Question - 2

A system of $n = 100$ moles of an ideal gas is taken through a **quasi-static reversible cyclic process** $A \to B \to C \to A$ depicted below on the Pressure-Volume phase plane.

Let
$$V(A) = 3 \text{ M}^3 \quad P(A) = 10^5 \text{ pa}$$
$$V(C) = 6 \text{ M}^3 \quad P(B) = 2 \times 10^5 \text{ pa}$$

Let D be the point on the phase diagram at which the temperature is maximum. Find the pressure, volume, and temperature at D. The entropy at the point A is taken as zero : $S(A) = 0$. Find the value of entropy at D.
$C_V = 3nR/2$; $C_P = 5nR/2$; $R = 8.31447$ joules (kelvin)$^{-1}$ (mol)$^{-1}$) **(12 Marks)**

Solution

- **Segment AB**

    Consider points on the line segment AB. The volume remains the same at 3 M^3; the pressure increases from 10^5 pa at A to 2×10^5 pa at B. The temperature is given by

    $$T = \frac{PV}{nR} = \frac{3P}{100R}$$

    Hence in this segment the temperature is maximum at B. We have

    $$T(B) = \frac{6 \times 10^5}{100R} = 721.634 \text{ kelvin.}$$

- **Segment AC**

  Consider points on the line segment AC. The pressure remains constant at 10^5 pa. The volume increases from 3 M^3 at A to 6 M^3 at C. The temperature is given by

  $$T = \frac{PV}{nR} = \frac{10^5 V}{nR}$$

  Hence in this segment, the temperature is maximum at C and is given by

  $$T(C) = \frac{6 \times 10^5}{100R} = 721.634 \text{ kelvin}$$

- **Segment BC**

  Consider points on the segment BC. The equation of the line passing through B and C can be formally written as
  $$P(V) = \alpha_1 V + \alpha_2$$
  The slope α_1 and the intercept α_2 can be calculated from the following linear equations.

  $$\begin{pmatrix} 3 & 1 \\ 6 & 1 \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \begin{pmatrix} 2 \times 10^5 \\ 10^5 \end{pmatrix}$$

  Solving the above

  $$\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = \begin{pmatrix} -1/3 & +1/3 \\ +2 & -1 \end{pmatrix} \begin{pmatrix} 2 \times 10^5 \\ 10^5 \end{pmatrix}$$

  We get

  $$\alpha_1 = -\frac{10^5}{3}; \quad \alpha_2 = 3 \times 10^5$$

  Thus on the segment BC

  $$P(V) = \alpha_1 V + \alpha_2$$

  $$T(V) = \frac{PV}{nR}$$

  $$= \frac{1}{nR} \left(\alpha_1 V^2 + \alpha_2 V \right)$$

  To determine the value of V at which T is extremum, we take the derivative with respect to V and set it to zero.

  $$\frac{dT}{dV} = \frac{1}{nR} \left(2\alpha_1 V + \alpha_2 \right) = 0$$

  Solving the above,

  $$V^\star = \frac{2\alpha_1}{\alpha_2} = 4.5 \text{ M}^3$$

Thus at $V = V^\star = 4.5$ M^3 the temperature is an extremum. To find if the extremum is maximum or minimum we take the second derivative and evaluate it at $V^\star$. We get,

$$\left.\frac{d^2T}{dV^2}\right|_{V^\star} = \frac{2\alpha_1}{nR}$$

$$= \text{negative since } \alpha_1 \text{ is negative}$$

Therefore at $V = V^\star = 4.5$ M^3 the temperature is maximum. We have

$$P^\star = P(V^\star) = \alpha_1 V^\star + \alpha_2 = 1.5 \times 10^5 \text{ pa}$$

At $D = (P^\star, V^\star)$ on the phase diagram, the temperature is maximum. We recognize

$$P^\star = \frac{P(B) + P(C)}{2}$$

$$V^\star = \frac{V(B) + V(C)}{2}$$

D is the midpoint of the line segment BC.

- **Temperature at D**

  In the phase diagram, the temperature is maximum at the point D. The temperature at D is given by

$$T(D) = \frac{P^\star V^\star}{nR}$$

$$= \frac{4.5 \times 1.5 \times 10^5}{100 \times 8.31447} = 811.838 \text{ kelvin}$$

- **Entropy at D**

  It is given that $S(A) = 0$. To calculate entropy at D we select a convenient path (reversible process) that takes us from A to D. Let E denote the midpoint od the segment AB. consider the path $A \to E \to D$.

6

P

B

E

D

A

C

V
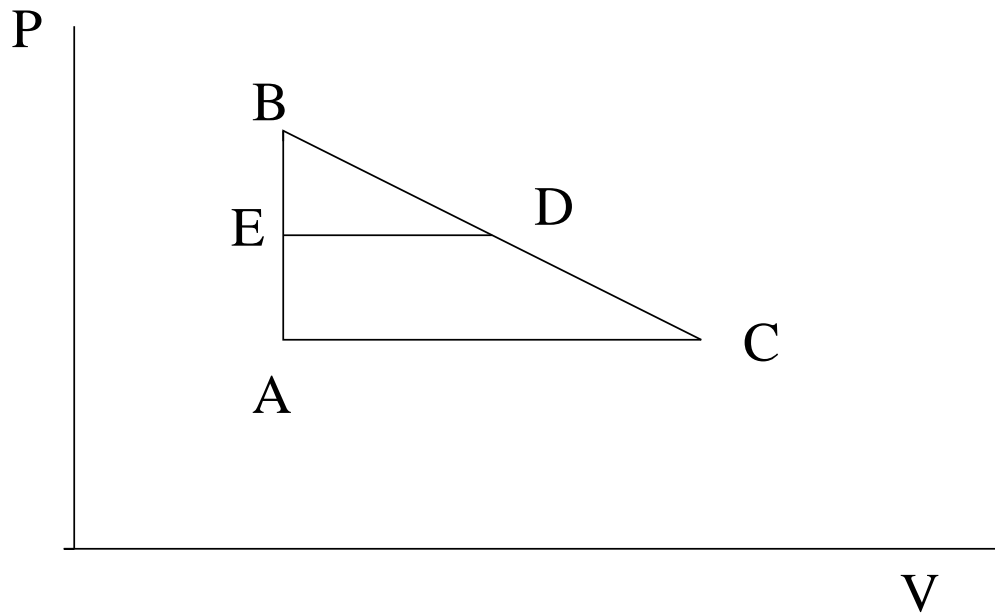
The process $A \rightarrow E$ is at constant volume; and the process $E \rightarrow D$ is at constant pressure. Therefore

$$S(D) = S(A) + C_V \int_{P(A)}^{P(E)} \frac{dP}{P} + C_P \int_{V(E)}^{V(D)} \frac{dV}{V}$$

$$= C_V \ln 1.5 + C_P \ln(4.5/3)$$

$$= \frac{nR}{2} \left[3 \ln 1.5 + 5 \ln(4.5/3) \right]$$

$$= 134.849 \text{ joules/kelvin}$$

- **Results in a nutshell**

$P(D)$	1.5×10^5 pa
$V(D)$	4.5 M³
$T(D)$	811.838 kelvin
$S(D)$	134.849 joules/kelvin

Question - 3

Consider a closed system of N non-interacting particles at temperature T Kelvin. Let $\epsilon = k_B T$ Joules. These particles occupy three non-degenerate energy levels :

- ground state of energy zero;
- first excited state of enegy ϵ Joules and
- second excited state of energy 2ϵ Joules.

The (canonical ensemble) average of energy is $10^{25}\epsilon$ Joules. The particles are identical and **distinguishable**. What is the value of N ? (6 Marks)

SOLUTION

$$Q(T, V, N) = [1 + \exp(-\beta\epsilon) + \exp(-2\beta\epsilon)]^N$$

$$\ln Q = N \ln [1 + \exp(-\beta\epsilon) + \exp(-2\beta\epsilon)]$$

$$U = \langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = \frac{\epsilon \exp(-\beta\epsilon) + 2\epsilon \exp(-2\beta\epsilon)}{1 + \exp(-\beta\epsilon) + \exp(-2\beta\epsilon)}$$

$$U = N\frac{\epsilon e^{-1} + 2\epsilon e^{-2}}{1 + e^{-1} + e^{-2}} = N\epsilon \frac{e + 2}{e^2 + e + 1}$$

It is given that $U = 10^{25}\epsilon$. Therefore,

$$N = 10^{25} \times \frac{e^2 + e + 1}{e + 2} = 2.354 \times 10^{25}.$$

Question - 4

Let $\{E_n = n\epsilon : n = 0, 1, 2, \cdots\}$, be the energy levels of a macroscopic closed system in equilibrium at $T = 300$ kelvin, where $\epsilon = 300\ k_B$ joules. The n-th energy level is $(n+1)$-fold degenerate. Calculate the entropy of the system. Write your answer to third decimal accuracy.
$(k_B = 1.381 \times 10^{-23})$

SOLUTION

$$E_n = n\epsilon; \quad g_n = n+1 \quad n = 0, 1, 2, \cdots$$

$$Q = \sum_{n=0}^{\infty} g_n \exp(-\beta E_n) = \sum_{n=0}^{\infty} (n+1) \exp(-\beta\epsilon\ n)$$

$$= \frac{1}{[1 - \exp(-\beta\epsilon)]^2}$$

$$\ln Q = -2 \ln[1 - \exp(-\beta\epsilon)]$$

$$\frac{\partial \ln Q}{\partial \beta} = \left[-\frac{2}{1 - \exp(-\beta\epsilon)} \right] [-\exp(-\beta\epsilon)] [-\epsilon]$$

$$U = \langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = \frac{2\epsilon \exp(-\beta\epsilon)}{1 - \exp(-\beta\epsilon)}$$

$$F = 2k_B T \ln[1 - \exp(-\beta\epsilon)]$$

$$S = \frac{U - F}{T} = \frac{2\epsilon \exp(-\beta\epsilon)}{T[1 - \exp(-\beta\epsilon)]} - 2k_B \ln[1 - \exp(-\beta\epsilon)]$$

$$= \frac{2(300 k_B)e^{-1}}{300(1 - e^{-1})} - 2k_B \ln(1 - e^{-1})$$

$$\frac{S}{k_B} = 2 + \frac{2}{e - 1} - 2\ln(e - 1)$$

$$= 2.081$$

$$S = 1.381 \times 2.081 \times 10^{-23}$$

$$= 2.874 \times 10^{-23} \text{ joules/kelvin}$$