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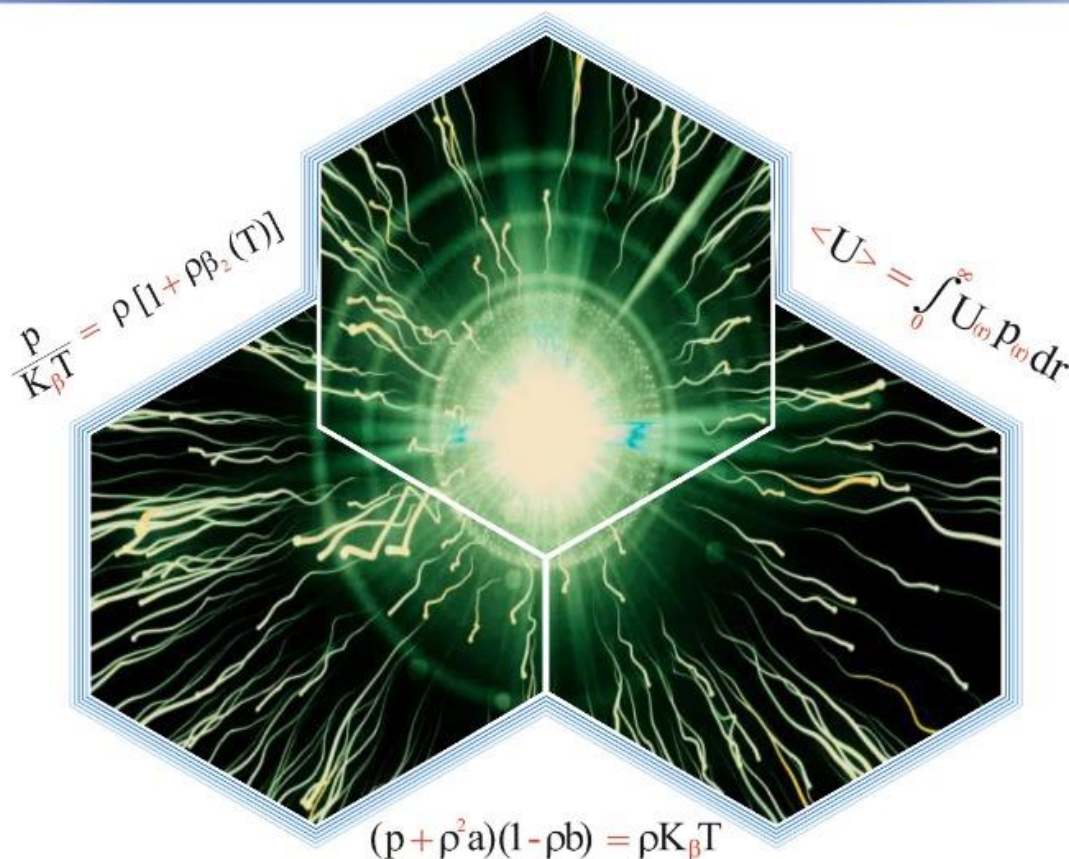
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TEACH YOURSELF

THERMAL & STATISTICAL PHYSICS

For BS/M.Sc Physics Programme

3rd Edition



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Prof. Dr. Anwar Manzoor Rana
Dr. Syed Hamad Bukhari

TEACH YOURSELF

**THERMAL &
STATISTICAL PHYSICS**

2nd Edition

For **BS/M.Sc Physics** students of all Pakistani Universities/Colleges

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Dr. Anwar Manzoor Rana

Department of Physics

Bahauddin Zakariya University, Multan

&

Dr. Syed Hamad Bukhari

Department of Physics

G.C. University Faisalabad, Sub-Campus, Layyah

•

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Chapter 1

Equilibrium Thermodynamics

SOLVED PROBLEMS

Problem: 1.1- Rewrite the van der Waals equation in the form $P = G(\theta_G, V)$.

Solution

The van der Waals equation is given by

$$\begin{aligned}\Rightarrow \quad \theta_G R &= \left(P + \frac{a}{V}\right) (V - b) \\ \frac{\theta_G R}{(V - b)} &= P + \frac{a}{V} \\ \text{or } P &= \frac{\theta_G R}{V - b} - \frac{a}{V} \quad \text{or } P = G(\theta_G, V)\end{aligned}$$

Problem: 1.2-

By writing the internal energy as a function of state $U(T, V)$ show that

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

Solution

$$U = U(T, V)$$

Differentiating it, we have

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (1.1)$$

As, from first law of thermodynamics: $dQ = dU + PdV$, so that

$$dU = dQ - PdV \quad (1.2)$$

putting value of Eq.(1.2) and Eq.(1.1), we have

$$\begin{aligned} dQ - PdV &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial T}\right)_T dV \\ dQ &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial T}\right)_T dV + PdV \\ dQ &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial T}\right)_T + P\right] dV \end{aligned}$$

Hence proved.

Problem: 1.3- Which one of the following is the exact differential?

1. $dx = (10y + 6z) dy + 6ydz$,
2. $dx = (3y^2 + 4yz) dy + (2yz + y^2) dz$,
3. $dx = y^4Z^{-1}dy + zdz$?

Solution

(1).

$$dx = (10y + 6z) dy + 6ydz$$

Let $dx = A dy + B dz$, where $A = 10y + 6z$ and $B = 6y$.

$$\text{If } \left(\frac{\partial A}{\partial z}\right)_y = \left(\frac{\partial B}{\partial y}\right)_z$$

then dx is an exact differential equation.

$$\begin{aligned} \left(\frac{\partial A}{\partial z}\right)_y &= \frac{\partial}{\partial z} (10y + 6z) = 6 \\ \left(\frac{\partial B}{\partial y}\right)_z &= \frac{\partial}{\partial y} (6y) = 6 \end{aligned}$$

Hence these are exact differentials.

(2).

$$dx = (3y^2 + 4yz) dy + (2yz + y^2) dz$$

Let $dx = A dy + B dz$, where $A = (3y^2 + 4yz)$ and $B = 2yz + y^2$. The given equation is an exact differential.

$$\text{If } \left(\frac{\partial A}{\partial z} \right)_y = \left(\frac{\partial B}{\partial y} \right)_z$$

Now

$$\left(\frac{\partial A}{\partial z} \right)_y = \frac{\partial}{\partial z} (3y^2 + 4yz) = 4y$$

$$\left(\frac{\partial B}{\partial y} \right)_z = \frac{\partial}{\partial y} (2yz + y^2) = 2z + 2y$$

$$\left(\frac{\partial A}{\partial z} \right)_y \neq \left(\frac{\partial B}{\partial y} \right)_z$$

Hence, this is not an exact differential.

(3).

$$dx = y^4 z^{-1} dy + z dz$$

Here $dx = A dy + B dz$, where $A = y^4 z^{-1}$ and $B = z$. The given equation is an exact differential.

$$\text{If } \left(\frac{\partial A}{\partial z} \right)_y = \left(\frac{\partial B}{\partial y} \right)_z$$

Let us check

$$\left(\frac{\partial A}{\partial z} \right)_y = \frac{\partial}{\partial z} \left(\frac{y^4}{z} \right) = -\frac{y^4}{z^2}$$

$$\left(\frac{\partial B}{\partial y} \right)_z = \frac{\partial}{\partial y} (z) = 0$$

So

$$\left(\frac{\partial A}{\partial z}\right)_y \neq \left(\frac{\partial B}{\partial y}\right)_z$$

is not an exact differential.

Problem: 1.4- The equation listed below are not exact differentials. Find for each equation an integrating factor $g(y, z) = y^\alpha z^\beta$, where α and β can be any number that will turn in into an exact differential.

1. $dx = 12z^2dy + 18yzdz$

2. $dx = 2e^{-z}dy - ye^{-z}dz$

Solution

(1).

$$\begin{aligned} dx &= g(y, z) [12z^2dy + 18yzdz] \\ \text{As } g(y, z) &= y^\alpha z^\beta \\ dx &= 12z^2y^\alpha z^\beta dy + 18yz y^\alpha z^\beta dz \\ dx &= 12y^\alpha z^{2+\beta} dy + 18y^{\alpha+1} z^{\beta+1} dz \end{aligned}$$

Here $dx = A dy + B dz$ so $A = 12y^\alpha z^{\beta+2}$ and $B = 18y^{\alpha+1} z^{\beta+1}$

$$\begin{aligned} \left(\frac{\partial A}{\partial z}\right)_y &= 12y^\alpha (\beta + 2) z^{\beta+1} \\ \left(\frac{\partial B}{\partial y}\right)_z &= 18z^{\beta+1} (\alpha + 1) y^\alpha \end{aligned}$$

dx is an exact differential, if $\left(\frac{\partial A}{\partial z}\right)_y = \left(\frac{\partial B}{\partial y}\right)_z$

$$\begin{aligned} \text{i.e., } 12y^\alpha (\beta + 2) z^{\beta+1} &= 18(\alpha + 1) z^{\beta+1} y^\alpha \\ 2(\beta + 2) &= 3(\alpha + 1) \\ 2\beta + 4 &= 3\alpha + 3 \\ 2\beta - 2\alpha + 1 &= 0 \\ \alpha &= \frac{2\beta + 1}{3} \text{ and } \beta = \frac{3\alpha - 1}{2} \end{aligned}$$

So, if $\beta = 1, \alpha = \frac{2+1}{3} = \frac{3}{3} = 1$. Hence, $\alpha = 1, \beta = 1$.

(2).

$$dx = g(y, z) [2e^{-z}dy - ydz e^{-z}]$$

$$dx = y^\alpha z^\beta (2e^{-z}dy - ye^{-z}dz)$$

$$dx = 2e^{-z}y^\alpha z^\beta dy - z^\beta y^{\alpha+1} e^{-z} dz = A dy + B dz$$

$$A = 2e^{-z}y^\alpha z^\beta \quad \text{and} \quad B = -e^{-z}y^{\alpha+1}z^\beta$$

Now, let dx is an exact differential, so $\left(\frac{\partial A}{\partial z}\right)_y = \left(\frac{\partial B}{\partial y}\right)_z$.

$$\begin{aligned} \text{Now, } \left(\frac{\partial A}{\partial z}\right)_y &= 2y^\alpha (e^{-z}(-1)z^\beta + e^{-z}\beta z^{\beta-1}) \\ &= 2y^\alpha (e^{-z}\beta z^{\beta-1} - e^{-z}z^\beta) \\ \left(\frac{\partial B}{\partial y}\right)_z &= \frac{\partial}{\partial y} (-e^{-z}y^{\alpha+1}z^\beta) \\ &= -e^{-z}(\alpha+1)y^\alpha z^\beta \end{aligned}$$

Now

$$\begin{aligned} -2y^\alpha e^{-z}z^\beta + 2y^\alpha (e^{-z}\beta z^{\beta-1}) &= -e^{-z}(\alpha+1)y^\alpha z^\beta \\ 2e^{-z}(\beta z^{\beta-1} - z^\beta) &= -e^{-z}(\alpha+1)z^\beta \quad \text{dividing by } y^\alpha \\ 2\beta z^{\beta-1} - 2z^\beta &= -(\alpha+1)z^\beta \quad \text{dividing by } e^{-z} \\ 2\beta z^{\beta-1} &= -(\alpha+1)z^\beta + 2z^\beta \\ 2\beta &= \frac{-(\alpha+1)z^\beta + 2z^\beta}{z^{\beta-1}} \\ 2\beta &= -\frac{((\alpha+1)+2)z^\beta}{z^{\beta-1}} \\ 2\beta &= \frac{(-\alpha-1+2)z^\beta}{z^{\beta-1}} \end{aligned}$$

$$\begin{aligned}
2\beta &= z(1 - \alpha) \\
\frac{2\beta}{z} &= 1 - \alpha \\
\frac{2\beta}{z} - 1 &= -\alpha \\
\alpha &= 1 - \frac{2\beta}{z} \\
\alpha &= \frac{z - 2\beta}{z}
\end{aligned}$$

So, if $\alpha = 1, \beta = 0$

Problem: 1.5- Differentiate

$$x = z^2 e^{y^2 z}$$

to get expression for $dx = Ady + Bdz$. Now divided by $ze^{y^2 z}$. Is the resulting equation an exact differential?

Solution

$$\begin{aligned}
dx &= Ady + Bdz \\
A &= \left(\frac{dx}{dy} \right)_z = z^2 e^{y^2 z} (2zy) = 2yz^3 e^{y^2 z} \\
B &= \left(\frac{dx}{dz} \right)_y = 2ze^{y^2 z} + z^2 e^{y^2 z} (y^2) = 2ze^{y^2 z} + y^2 z^2 e^{y^2 z} \\
dx &= 2yz^3 e^{y^2 z} dy + (2ze^{y^2 z} + y^2 z^2 e^{y^2 z}) dz
\end{aligned}$$

Now divided by $ze^{y^2 z}$, we get

$$dx = 2yz^2 dy + (2 + y^2 z) dz = A' dy + B' dz$$

Now, $A' = 2yz^2, B' = 2 + y^2 z$

$$\left(\frac{\partial A'}{\partial z} \right)_y = 4yz$$

$$\left(\frac{\partial B'}{\partial y}\right)_z = 2yz$$

It is not an exact differential, because $\left(\frac{\partial A'}{\partial z}\right)_y \neq \left(\frac{\partial B'}{\partial y}\right)_z$.

Chapter 2

Elements of Probability Theory

SOLVED PROBLEMS

Problem: 2.1- Two drunks start out together at the origin each having equal probability of making step to the left or right along x -axis. Find the probability they meet again after N -step. It is to be understood that the men make their steps simultaneously.

Solution

We consider the relative motion of two drunks, with each simultaneous step, they have probability of $\frac{1}{4}$ of decreasing their separation and $\frac{1}{4}$ of increasing their separation. Let the number of times each case occurs n_1, n_2 and n_3 respectively.

$$W(n_1, n_2, n_3) = \frac{N!}{n_1!n_2!n_3!} \left(\frac{1}{4}\right)^{n_1} \left(\frac{1}{4}\right)^{n_2} \left(\frac{1}{4}\right)^{n_3}$$

Where $n_1 + n_2 + n_3 = N$.

The drunk meets if $n_1 = n_2$ the probability that they meet after N -steps irrespective of the number of step n_3 which leave their separation unchanged,

$$P = \sum_{n_3=0}^N \frac{N!}{n_1!n_2!n_3!} \left(\frac{1}{4}x\right)^{n_1} \left(\frac{1}{4}x\right)^{n_2} \left(\frac{1}{2}\right)^{n_3}$$

Where we have inserted a parameter x which cancels if $n_1 = n_2$.

By Binomial expansion

$$P' = \left(\frac{1}{4}x + \frac{1}{4}x + \frac{1}{2}\right)^N = \left(\frac{1}{2}\right)^{2N} (x^{1/2} + x^{-1/2})^{2N}$$

Now

$$P' = \left(\frac{1}{2}\right)^{2N} \sum_n \frac{2N!}{n!(2N-n)!} (x^{1/2})^n (x^{-1/2})^{2N-n}$$

Since x cancel, we choose the term where $n = 2N - n$ or $N = n$.

$$P = \left(\frac{1}{2}\right)^{2N} \frac{(2N)!}{(N!)^2}$$

Problem: 2.2- A penny is tossed 400 times. Find the probability of getting 220 heads.

Solution

We use the Gaussian approximation to Binomial distribution.

$$W(n) = \frac{1}{\sqrt{2\pi \frac{400}{4}}} e^{-\frac{(220-200)^2}{2(400/4)}}$$

$$W(n) = (0.0399)e^{-(20/200)}$$

$$W(n) = (0.0399)e^{-(0.1)}$$

$$W(n) = (0.0399)(0.9048)$$

$$W(n) = 0.0361$$

Problem: 2.3- Consider a random walk problem in 1D, the probability of displacement between S and $S + dS$ being

$$w(S)dS = (2\pi S^2)^{-\frac{1}{2}} e^{-(S-l)^2/2S^2}$$

After N -steps. What is dispersion $(x - \hat{x})^2$?

Solution

$$(x - \bar{x})^2 = \sum_i^N (\overline{S_i - l})^2 + \sum_{j+i}^N \sum_i^N (\overline{S_i - l})(\overline{S_i - l})$$

Where $(\overline{S_i - l}) = l - l = 0$

To find the dispersion $(\overline{S_i - l})^2$ we note the probability that step length is between S and $S + ds$ in the $\frac{ds}{2b}$.

$$(\overline{S_i - l})^2 = \int_{l-b}^{l+b} \frac{(\overline{S_i - l})^2 ds_i}{2b} = \frac{b^2}{3}$$

Since $(x - \bar{x})^2 = \sum_i^N S^2 = NS^2$

Problem: 2.4- Suppose that preceding problem the volume V under consideration such that $0 \ll \frac{V}{V_o} \ll 1$. What is the probability that the number of molecules in the volume between N and $N + dN$.

Solution

Since $\frac{V}{V_o} \ll 1$ and N_o is large. We use Gaussian distribution

$$P(N)dN = \frac{1}{\sqrt{2\pi\Delta\bar{N}^2}} \exp\left(\frac{-(N - \bar{N})^2}{2\Delta\bar{N}^2}\right) dN$$

Problem: 2.5- A pair of six faced dice with faces marked form 1 to 6 each thrown simultaneously. What is the probability that sum of numbers which shown up is 6.

Solution

No. of ways in which 1st dice can fall $n_1 = 6$.

No. of ways in which 2nd dice can fall $n_2 = 6$.

Total number of equally likely ways in which dice can fall.

$$N = n_1 \times n_2$$

$$N = 6 \times 6 = 36$$

These 36 ways given by

$$(1, 1)(1, 2)(1, 3)(1, 4)(1, 5)(1, 6)$$

$$(2, 1)(2, 2)(2, 3)(2, 4)(2, 5)(2, 6)$$

$$(3, 1)(3, 2)(3, 3)(3, 4)(3, 5)(3, 6)$$

$$(4, 1)(4, 2)(4, 3)(4, 4)(4, 5)(4, 6)$$

$$(5, 1)(5, 2)(5, 3)(5, 4)(5, 5)(5, 6)$$

$$(6, 1)(6, 2)(6, 3)(6, 4)(6, 5)(6, 6)$$

It is clear from above number of ways, in which two dice can fall with sum of numbers equal to 6 is number of favorable ways is equal to 5. Required probability

$$P = \frac{m}{n}$$

$$P = \frac{5}{36}$$

Problem: 2.6- Specific heat of 4.25kg/k Boltzmann constant $k = 1.3851k$. Calculate the ratio of numbers of accessible microstates to 1gm of water at 300K and 300.001K.

Solution

$$\text{Mass of water } m = 1gm$$

Specific heat of water = 4.25 J/mol/K

Initial temperature = 300 K

Final temperature $T + dT = 300.001$ K

Rise of temperature = $(T + dT) - T = dT$

$$= 300.001 - 300 = 0.0001 = 10^{-4} \text{ K}$$

Heat gained by water

$$\begin{aligned} \Delta Q &= mCdT \\ &= 1 \times 4.2 \times 10^{-4} \\ &= 4.2 \times 10^{-4} \text{ J} \end{aligned}$$

Change in entropy

$$\begin{aligned} \Delta S &= \frac{\Delta Q}{T} \\ &= \frac{4.2 \times 10^{-4}}{300} \\ &= 1.4 \times 10^{-6} \text{ Jk}^{-1} \end{aligned}$$

As

$$\begin{aligned} \ln \left(\frac{W_2}{W_1} \right) &= \frac{\Delta S}{k} \\ \ln \left(\frac{W_2}{W_1} \right) &= \frac{1.4 \times 10^{-6}}{1.38 \times 10^{-23}} \\ \ln \left(\frac{W_2}{W_1} \right) &= 1.01 \times 10^{17} \end{aligned}$$

Chapter 3

Formulation of Statistical Methods

SOLVED PROBLEMS

Problem: 3.1- Write an expression for partition function z if the particle obeys Maxwell-Boltzmann distribution. Consider a system having two particles, each one can be in any one of three Quantum states $0, \varepsilon$ and 3ε . The system is in contact with heat reservoir.

Solution

To find the Maxwell-Boltzmann statics, the table for configuration is

Configuration			No. of states
0	ε	3ε	MB
xx			1
	xx		1
		xx	1
x	x		2
x		x	2
	x	x	2

From table the partition function for Maxwell-Boltzmann statistics will be:

$$Z_{MB} = 1 + e^{-2\varepsilon\beta} + e^{-6\varepsilon\beta} + 2e^{-\varepsilon\beta} + 2e^{-3\varepsilon\beta}$$

Problem: 3.2- The calculation involving Fermi-Dirac statistics gives rise to integral I_m . Show that all these integral can be evaluated

$$J(k) = \int_{-\infty}^{\infty} \frac{e^{ikx} dx}{(e^x + 1)(e^{-x} + 1)}$$

Since power series $J(k)$ yields

$$J(k) = \sum_{n=0}^{\infty} \frac{(ik)^m}{m!} I_m$$

Solution

We expand e^{ikx} in the integral

$$\begin{aligned} J(k) &= \int_{-\infty}^{\infty} \frac{e^{ikx} dx}{(e^x + 1)(e^{-x} + 1)} \\ &= \int_{-\infty}^{\infty} \frac{e^x e^{ikx} dx}{(e^x + 1)^2} \\ &= \int_{-\infty}^{\infty} \frac{e^x dx}{(e^x + 1)^2} \sum_{m=0}^{\infty} \frac{(ik)^m}{m!} x^m \end{aligned}$$

Integrating the sum the yields

$$\begin{aligned} J(k) &= \frac{(ik)^m}{m!} \int_{-\infty}^{\infty} \frac{e^x}{(e^x + 1)^2} x^m dx \\ &= \sum_{m=0}^{\infty} \frac{(ik)^m}{m!} I_m \end{aligned}$$

Problem: 3.3- Radiation from the Big Bang has been doppler shifted to longer wavelength by expansion of universe today has a spectrum corresponding to that of a black-body at 2.7K. Find the wave-length.

Solution

From Wein's displacement law, we have

$$\begin{aligned}\lambda_{max} &= \frac{2.898 \times 10^{-3} mK}{T} \\ &= \frac{2.898 \times 10^{-3} mK}{2.7K} \quad \text{Given } T = 2.7K \\ &= 1.1 \times 10^{-3} m\end{aligned}$$

Problem: 3.4- A dielectric solid has an index of refraction n_o . Which can be assumed to be constant up to infrared frequency. Calculate the contribution of black body radiation in solid heat capacity at temperature $T = 300^\circ K$. Compare this result with the classical lattice heat capacity of $3R$ per mole.

Solution

The energy of a black body radiation in dielectric

$$\bar{F} = V\bar{\mu} = V \frac{\pi^2 (k_B T)^4}{15 (c\hbar)^3}$$

Where c is the velocity of light in the material c .

$$\begin{aligned}\bar{F} &= V \frac{\pi^2 (k_B T)^4}{15 (c\hbar)^3} n_o^3 \\ &= \frac{4\sigma n_o^3 V T^4}{c}\end{aligned}$$

Thus Stephen-Boltzmann constant

$$\sigma = \frac{\pi^2 k^4}{60c^2 \hbar^3}$$

Thus

$$C_v = \left(\frac{\partial \bar{F}}{\partial T} \right)_v = \frac{16\sigma n_o^3 VT^3}{c}$$

Taking its ratio with $C_V = 3R$ gives

$$\frac{C_{v'}}{C_v} = \frac{16\sigma n_o^3 VT^3}{3R}$$

For an order of magnitude calculation we can let $V = 10\text{cm}^3/\text{mol}$ and $n_o = 1.5$.

At 300K we find

$$\frac{C_{v'}}{C_v} \approx 10^{-13}$$

Problem: 3.5- An electron in one dimensional infinite potential well defined by $V(x) = 0$ for $-a \leq x \leq a$ and $V(x) = \infty$ otherwise goes from the $n = 4, n = 2$ level. The frequency of emitted photon is $3.43 \times 10^{14}\text{Hz}$. Find the width of box.

Solution

$$E_n = \frac{\pi^2 \hbar^2 n^2}{8ma^2}$$

Given that $n = 1, n = 2$

$$\begin{aligned} E_1 - E_2 &= \frac{12\pi^2 \hbar^2}{8ma^2} \\ h\nu &= \frac{12\pi^2 \hbar^2}{8ma^2} \quad \because E_1 - E_2 = h\nu \\ a^2 &= \frac{12\pi^2 \hbar^2}{8m\hbar\nu} \\ a^2 &= \frac{3\hbar^2}{8m\hbar\nu} = \frac{3\hbar}{8m\nu} \\ a^2 &= \frac{3(6.626 \times 10^{-34}\text{Js})}{8(9.1 \times 10^{-31})(3.43 \times 10^{14})} \\ a^2 &= 79.6 \times 10^{-20}\text{m}^2 \\ a &= 8.92 \times 10^{-10}\text{m} \end{aligned}$$

Chapter 4

Partition Function

SOLVED PROBLEMS

Problem: 4.1- A system consists of three energy levels i.e., ground level $E_0 = 0J$, $E_1 = 0.25k_B T J$ and $E_2 = 0.77k_B T J$. Calculate the partition function, also calculate the probability of 2nd energy level.

Solution

Partition function: Let z is the partition function

$$z = \sum_i e^{-\beta E_i}$$

Where $\beta = \frac{1}{k_B T}$, Now

$$z = \exp\left(\frac{-1}{k_B T}(0)\right) + \exp\left(\frac{-1}{k_B T}(0.25)k_B T\right) + \exp\left(\frac{1}{k_B T}(0.77)k_B T\right)$$

$$z = e^0 + e^{-0.25} + e^{-0.77}$$

$$z = 1 + 1.2418 \quad e^0 = 1$$

$$z = 2.2418$$

Which is partition function.

Probability:

$$P(E) \propto e^{-E/k_B T}$$

$$P(E) = \frac{e^{-E_2/k_B T}}{e^{-E_0/k_B T} + e^{-E_1/k_B T} + e^{-E_2/k_B T}}$$

Putting the values

$$P(E) = \frac{e^{\frac{-0.77k_B T}{k_B T}}}{e^{\frac{-0k_B T}{k_B T}} + e^{\frac{-0.25k_B T}{k_B T}} + e^{\frac{-0.77k_B T}{k_B T}}}$$

$$P(E) = \frac{e^{-0.77}}{e^0 + e^{-0.25} + e^{-0.77}}$$

$$P(E) = \frac{0.46301}{1 + 0.77880 + 0.46301}$$

$$P(E) = \frac{0.46301}{2.24184} = 0.20653$$

Problem: 4.2- Determine the probability of an energy state above E_F occupied by an electron. Determine the probability that energy level $3k_B T$ above the Fermi-energy level is occupied by an electron.

Solution

$$f_E(E) = \frac{1}{1 + e^{(E-E_F/k_B T)}}$$

Putting values

$$f_E = \frac{1}{1 + e^{(3k_B T/k_B T)}}$$

$$f_E = \frac{1}{1 + e^3}$$

$$f_E = \frac{1}{1 + 20.08554}$$

$$f_E = \frac{1}{21.08554} = 0.04743$$

An energies above E_F the probability of state being occupied by an electron can becomes significantly less then unity.

Problem: 4.3- Assume a Fermi-energy level exactly in the center of bandgap energy of a Semi-conductor at $T = 300K$. Calculate the probability that energy of a state in bottom.

Solution

Since

$$\begin{aligned} E - E_F &= E_c - E_F \\ 0.56 &\gg k_B T \end{aligned}$$

We can use the Boltzmann approximation

$$\begin{aligned} f(E) &= \frac{1}{1 + e^{(E-E_F)/k_B T}} \\ &\approx \frac{1}{e^{(E-E_F)/k_B T}} \\ &= e^{-(E-E_F)/k_B T} \\ &= e^{(E+E_F)/k_B T} \\ &= e^{-\frac{0.56\text{eV}}{0.002580}} \\ &= 3.938 \times 10^{-10} \end{aligned}$$

Problem: 4.4- Harmonic oscillator/canonical ensemble. Consider a system of N harmonic oscillators. Which are indistinguishable, one dimensional and having same frequency ω .

(a) Compute partition function.

(b) Find free energy.

Solution

A system of N non-integrating independent distinguishable, in thermal equilibrium at absolute temperature,

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

Partition function:

$$\begin{aligned}
 z_1(T, V) &= \frac{1}{n} \int e^{-\beta P^2/2m} e^{-\beta m\omega^2 x^2/2} dx dp \\
 z_1(T, V) &= \frac{1}{n} \int_{-\infty}^{\infty} e^{-\beta P^2/2m} dp \int_{-\infty}^{\infty} e^{-\beta m\omega^2 x^2/2} dx \\
 z_1(T, V) &= \frac{4}{n} \left[\frac{\sqrt{\pi}}{2} \frac{1}{(\beta/2m)^{1/2}} \right] \left[\frac{\sqrt{\pi}}{2} \frac{1}{(\beta m\omega^2/2)^{1/2}} \right] \\
 z_1(T, V) &= \frac{k_B T}{\hbar\omega}
 \end{aligned}$$

Partition function for whole system

$$z(T, V) = (z_1)^N = \left(\frac{k_B T}{\hbar\omega} \right)^N$$

Free energy:

$$\begin{aligned}
 A &= -k_B T \ln z \\
 A &= -k_B T \ln \left[\frac{k_B T}{\hbar\omega} \right] \\
 A &= N k_B T \ln \left(\frac{\hbar\omega}{k_B T} \right)
 \end{aligned}$$

Problem: 4.5- Calculate the probability of Harmonic oscillator $E_n = (n + \frac{1}{2}) \hbar\omega$ in state with n odd number if the oscillator is in contact with heat bath at temperature T .

Solution

The probability that the harmonic oscillator is in state with n -odd numbers is given by

$$\begin{aligned}
 P \left(n + \frac{1}{2} \right) &= \frac{\sum_{n=1}^{\infty} e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}} \\
 &= \frac{\sum_{n=1}^{\infty} e^{-\beta (n+\frac{1}{2})\hbar\omega}}{\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}}
 \end{aligned}$$

By expansion

$$\begin{aligned} & \frac{e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2} + e^{-5\beta\hbar\omega/2} + e^{-7\beta\hbar\omega/2} + \dots + \infty}{1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + e^{-3\beta\hbar\omega} + \dots + \infty} \\ &= \frac{e^{-\beta\hbar\omega} / (1 + e^{-2\beta\hbar\omega})}{1 / (1 + e^{-\beta\hbar\omega})} \\ &= \frac{e^{-\beta\hbar\omega} (1 - e^{-\beta\hbar\omega})}{1 - e^{-2\beta\hbar\omega}} \\ &= \frac{e^{-\beta\hbar\omega} - e^{-2\beta\hbar\omega}}{1 - e^{-2\beta\hbar\omega}} \end{aligned}$$

By simplifying it can be written as

$$P = \frac{e^{\beta\hbar\omega} - 1}{e^{2\beta\hbar\omega}}$$

$$P \left(n + \frac{1}{2} \right) = \frac{e^{\beta\hbar\omega} - 1}{e^{2\beta\hbar\omega} - 1}$$

Chapter 5

Statistical System

SOLVED PROBLEMS

Problem: 5.1- N non-interacting bosons are in an infinite potential well defined by $V(x) = 0$ for $0 < x < a$; $V(x) = \infty$ for $x < 0$ and $x > a$. Find the ground state energy of system. What would be the ground state energy if the particles are fermions.

Solution

The energy eigenvalue of a particle in infinite square well is given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

As the particles are Bosons N -particles will be in $n = 1$ state, total energy

$$E_{n_1, n_2, n_3, \dots, n_\gamma} = \frac{\pi^2 \hbar^2}{2a^2 m} (1^2 + 1^2 + 1^2 + \dots + 1^2)$$
$$E = \frac{\pi^2 \hbar^2}{2a^2 m} N$$

If particle are fermions a state can have only two of them one spin up and another spin down. Therefore, lowest state $N/2$ will be filled.

$$2E_1, 2E_2, 2E_3, \dots, E_{N/2} = E' = \frac{\pi^2 \hbar^2}{2ma^2} (1^2 + 1^2) + (2^2 + 2^2 + \dots) \dots$$
$$E^o = \frac{\pi^2 \hbar^2 N^3}{24ma^2}$$

Problem: 5.2- Calculate the root mean square speed if nitrogen at $27^{\circ}C$. Given $N = 6 \times 10^{23}$ molecules/mole, $k_B = 1.38 \times 10^{-16}$ ergs/k.

Solution

$$\text{Temperature} = T = 27 + 273 = 300K$$

$$\text{Mass of Nitrogen molecule} = m = \frac{\text{Mol.Wt}}{N} = \frac{28}{6 \times 10^{23}}$$

$$m = 4.66 \times 10^{-23} gm$$

$$V_{rms} = \sqrt{\frac{3kT}{m}}$$

Putting the values, where k is Boltzmann constant

$$\begin{aligned} V_{rms} &= \sqrt{\frac{3 \times 1.38 \times 10^{-16} \times 300}{4.66 \times 10^{-23}}} \\ &= \sqrt{26.65 \times 10^8} \\ &= 5.16 \times 10^4 \text{ cm/sec} \end{aligned}$$

Problem: 5.3- Draw the energy levels, including the spin orbit interaction for $n = 3$ and $n = 2$, state of Hydrogen atom and calculate the spin orbit double separation of the $2p$, $3p$ and $3d$ state. The Redberg constant of Hydrogen is $1.097 \times 10^7 m^{-1}$.

Solution

As we know that the energy levels for $n = 3$ and $n = 2$ states of Hydrogen ($z = 1$) including the spin orbit interaction.

The double separation

$$\Delta E = \frac{z^4 a^2 R}{n^3 (l + 1)}$$

For $2p$ state, $n = 2l$, $l = 1$

$$(\Delta E)_{2p} = \frac{(1/137)^2(1.097 \times 10^7)}{8 \times 2}$$

$$(\Delta E)_{2p} = 36.53m^{-1}$$

For 3p state $n = 3$, $l = 1$

$$(\Delta E)_{3p} = \frac{(1/137)^2(1.097 \times 10^7)}{27 \times 2}$$

$$= 10.82m^{-1}$$

For 3d state $n = 3$, $l = 2$

$$(\Delta E)_{3d} = \frac{(1/137)^2(1.097 \times 10^7)}{27 \times 3 \times 2}$$

$$= 3.61m^{-1}$$

Problem: 5.4- Consider an ideal gas of N -electrons in volume V at absolute zero.

(a) Calculate the total mean energy \bar{E} of this gas.

(b) Express \bar{E} in term of Fermi energy μ .

Solution

(a)

At $T = 0$ all states are filled up the energy μ . Hence mean number of particle per state is just 1. We have

$$\bar{E} = \int_0^\mu E n(E) dE$$

$$\text{As } n(E)dE = \frac{2V}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^2} e^{1/2} dE$$

Where the factor 2 is introduced since electrons have two spin states

$$\bar{E} = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^2} \int_0^\mu e^{3/2} dE$$

$$\bar{E} = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^2} \mu^{5/2}$$

(b)

Since

$$\mu = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{\gamma} \right)^{3/2}$$

So we have

$$\bar{E} = \frac{3}{5} N \mu$$

Which is our required result.

Problem: 5.5- A quark having one-third the mass of a proton is confined in a cubical box of side $1.8 \times 10^{-15}m$. Find the excitation energy in *Mev* form the first excited state to the second excited state.

Solution

$$E_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2ma^2} (n_1^2 + n_2^2 + n_3^2)$$

And

$$\text{First excited state } E_{211} = E_{121} = E_{112} = \frac{6\pi^2 \hbar^2}{2ma^2}$$

$$\text{First excited state } E_{221} = E_{212} = E_{122} = \frac{9\pi^2 \hbar^2}{2ma^2}$$

$$m = \frac{1.67262 \times 10^{-27}}{3}$$

$$m = 0.55754 \times 10^{-27} kg$$

$$\Delta E = \frac{3\pi^2 \hbar^2}{2ma^2}$$

$$\Delta E = \frac{3(3.14)^2 (1.05 \times 10^{-34})^2}{2(0.55754 \times 10^{-27} kg)(1.8 \times 10^{-15})^2}$$

$$\Delta E = 9.0435 \times 10^{-11} J$$

$$\Delta E = \frac{9.0435}{1.6 \times 10^{-19} J/eV}$$

$$\Delta E = 565.2 MeV$$

Chapter 6

Statistical Mechanics of Interacting System

SOLVED PROBLEMS

Problem: 6.1- Use the Debye approximation to find the following thermodynamics functions of a solid as a function of absolute temperature T .

- (a) $\ln z$, where z is partition function.
- (b) The mean energy.

Solution

Partition function:

As

$$\ln z = \beta N_{\eta} - \int_0^{\infty} \ln \left(1 - e^{-\beta \frac{1}{2} m \omega} \right) \delta_D(\omega) d\omega$$

Where

$$\delta_D(\omega) \begin{cases} \frac{3V}{2\pi^2} e^3 \omega^2 & \text{For } \omega < \omega_D \\ 0 & \text{For } \omega > \omega_D \end{cases}$$

Put

$$V = 6\pi^2 N \left(\frac{C}{\omega_D} \right)$$

We find

$$\ln z = \beta N_\eta - 9 \frac{N}{\omega_D} \int_0^{\omega_D} \ln(1 - e^{\beta t \omega}) \omega^2 d\omega$$

In terms of dimensionless variables $x = \beta \hbar \omega$ and $y = \beta \hbar \omega$, this gives

$$\begin{aligned} \ln z &= \frac{\partial N_\eta}{\hbar \omega_D} - \frac{9N}{Y^3} \int_0^y \ln(1 - e^x) x^2 dx \\ \ln z &= Y \frac{N_\eta}{\hbar \omega_D} - \frac{9N}{Y^3} \left[\ln(1 - e^{-x}) \frac{x^3}{3} \right]^y - \frac{1}{3} \int_0^y \frac{x^3 dx}{e^x - 1} \\ \ln z &= y \frac{N_\eta}{\hbar \omega_D} - 3N \ln(1 - e^{-y}) + N_D(y) \\ \ln z &= \frac{N_\eta}{\hbar \omega_D} - 3N \ln(1 - e^{-\theta_D/T}) + N_D \left(\frac{\theta_D}{T} \right) \end{aligned}$$

Where $k\theta_D = \hbar\omega_D$.

Free energy:

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln z = -\hbar \omega_D \frac{\partial}{\partial y} \ln z$$

Here

$$\begin{aligned} \bar{E} &= -N_\eta + \frac{3N}{\beta} Dy \quad \because Dy = D \left(\frac{\theta_D}{T} \right) \\ \bar{E} &= -N_\eta + 3NkTD \left(\frac{\theta_D}{T} \right) \end{aligned}$$

Problem: 6.2- Using heat of vaporization for water in J/g . Calculate the energy needed to boil $50.0g$ of water at its boiling point of $100^{\circ}C$

Solution

$$\text{The mass of water} = m = 50.0g$$

$$\text{Heat of vaporization} = Q = 2259 J/g$$

We have to find the energy is required to boil the involved amount of water

$$E = Qm$$

$$E = (50)(2259)$$

$$E = 112950J$$

$$E = 113 \times 10^3 J$$

$$E = 113 kJ$$

Problem: 6.3- What is the measured pressure of 10 moles of O_2 gas in $5L$ container at $30^{\circ}C$ by using van der Waals equation.

Solution

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

Given

$$n = 10 \text{ moles}$$

$$T = 30^{\circ}C = 303K$$

$$V = 5L$$

Putting values

$$P = \frac{(10)(303)(8.314)}{5}$$

$$P = \frac{25191.42}{5}$$

$$P = 5038.2 \text{ Pa}$$

$$P = 5.03 \times 10^3 \text{ Pa}$$

Problem: 6.4- One mole of a gas obeys van der Waals equation of state

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

and its internal energy is $U = cT - \frac{a}{V}$. Where a, b, c and R are constants. Calculate C_V

Solution

$U = \text{function of } (T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dU = dQ - PdV$$

Therefore

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = C$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_P = \frac{P}{\left(P - \frac{2a}{V^3}\right)(V - b) - b\left(P - \frac{a}{V^2}\right)}$$

Problem: 6.5- Determine the 2nd nearest neighbor distance for N_i at 100°C of its density at temp is 8.83 km^3 .

Solution

$$N_i, n = 4$$

$$\text{atomic weight} = 58.70 \text{ g/mol}$$

$$\rho = 8.83 \text{ g/cm}^3$$

Now

$$\frac{\text{Atomic weight}}{\rho} \times 10^{-6} = \frac{N_A}{n} \times a^3$$

$$a^3 = \frac{(58.7)(10^{-6})(4)}{(6.023 \times 10^{23})(8.83)}$$

$$a = 4.41 \times 10^{-29} \text{ m}^3$$

$$a = 3.61 \times 10^{-10} \times \frac{10^{12}}{\text{m}} \text{ pm}$$

$$a = 3.61 \times 10^2 \text{ pm}$$

Chapter 7

Advanced Topics

SOLVED PROBLEMS

Problem: 7.1- Use density matrix and trace to calculate the probability of obtaining state measurement.

Solution

If we perform a Von. Neumann measurement of state $\{(q_k|\psi_k)\}$ w.r.t a basis containing $|\phi\rangle$ the probability obtaining $|\phi\rangle$ is

$$\begin{aligned}\sum_k q_k |\langle \psi_k | \phi \rangle|^2 &= \sum_k q_k \text{Tr}(|\psi_k\rangle\langle\phi_k| |\phi\rangle\langle\phi|) \\ \sum_k q_k |\langle \psi_k | \phi \rangle|^2 &= \text{Tr} \left\{ \sum_k q_k |\psi_k\rangle\langle\phi_k| |\phi\rangle\langle\phi| \right\} \\ \sum_k q_k |\langle \psi_k | \phi \rangle|^2 &= \text{Tr}(\rho |\phi\rangle\langle\phi|)\end{aligned}$$

The same state.

Problem: 7.2- show that

$$\hat{\rho} = \frac{1}{2}|+n\rangle\langle+n| + \frac{1}{2}|-n\rangle\langle-n| = \frac{1}{2}|+z\rangle\langle+z| + \frac{1}{2}| - z\rangle\langle - z|$$

Where

$$\begin{aligned}
|+n\rangle &= \cos\left(\frac{\theta}{2}\right)|+z\rangle + e^{i\theta}\sin\left(\frac{\theta}{2}\right)|-z\rangle \\
|-n\rangle &= \sin\left(\frac{\theta}{2}\right)|+z\rangle - e^{-i\theta}\cos\left(\frac{\theta}{2}\right)|-z\rangle
\end{aligned}$$

Solution

Given density operator is

$$\hat{\rho} = \frac{1}{2}|+n\rangle\langle+n| + \frac{1}{2}|-n\rangle\langle-n|$$

Substituting the value of $|+n\rangle$ and $|-n\rangle$ yield,

$$\begin{aligned}
\hat{\rho} &= \frac{1}{2} \left[\left(\cos\left(\frac{\theta}{2}\right)|+z\rangle + e^{i\theta}\sin\left(\frac{\theta}{2}\right)|-z\rangle \right) \cdot \left(\langle+n| \cos\left(\frac{\theta}{2}\right) + \langle-z| e^{i\theta}\sin\left(\frac{\theta}{2}\right) \right) \right] \\
&\quad + \frac{1}{2} \left[\left(\sin\left(\frac{\theta}{2}\right)|+z\rangle - e^{-i\theta}\cos\left(\frac{\theta}{2}\right)|-z\rangle \right) \cdot \left(\langle+n| \sin\left(\frac{\theta}{2}\right) + \langle-z| e^{i\theta}\cos\left(\frac{\theta}{2}\right) \right) \right] \\
\hat{\rho} &= \left[\frac{1}{2} \right] \cos^2\left(\frac{\theta}{2}\right)|+z\rangle\langle+z| + e^{-i\theta}\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right)|+z\rangle\langle-z| \\
&\quad + e^{i\theta}\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right)|-z\rangle\langle+z| + e^{i\theta}e^{-i\theta}\sin^2\left(\frac{\theta}{2}\right)|-z\rangle\langle-z| \\
&\quad + \sin^2\left(\frac{\theta}{2}\right)|+z\rangle\langle+z| - e^{-i\theta}\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right)|+z\rangle\langle+z| \\
&\quad - e^{i\theta}\cos\left(\frac{\theta}{2}\right)\sin\left(\frac{\theta}{2}\right)|+z\rangle\langle+z| + e^{i\theta}e^{-i\theta}\cos^2\left(\frac{\theta}{2}\right)|+z\rangle\langle+z|
\end{aligned}$$

Now we are left with following expression

$$\begin{aligned}
\hat{\rho} &= \frac{1}{2} \left[\cos^2\left(\frac{\theta}{2}\right) + \sin^2\left(\frac{\theta}{2}\right) \right] |+z\rangle\langle+z| \\
&\quad + \frac{1}{2} \left[\cos^2\left(\frac{\theta}{2}\right) + \sin^2\left(\frac{\theta}{2}\right) \right] |-z\rangle\langle-z| \\
\hat{\rho} &= \frac{1}{2}|+z\rangle\langle+z| + \frac{1}{2}|-z\rangle\langle-z|
\end{aligned}$$

That is required result.

Problem: 7.3- Evaluate the behavior of internal energy and specific heat of Bosons gas in vicinity of Einstein condensation.

Solution

Let us define the function $g_\alpha z$ for $\alpha > 0$ and $|z| < 1$ by the series.

$$g_\alpha z = \sum_{k=1}^{\infty} \frac{z^k}{k^\alpha}$$

The function has the integral representation

$$g_\alpha z = \frac{1}{\Gamma(\alpha)} \int_0^\infty dx x^{\alpha-1} \frac{ze^{-x}}{1 - ze^{-x}}$$

Γ_α is Euler gamma function

$$\rho = \frac{1}{\lambda_B^3(T_o)}$$

$$\lambda_B(T) = \left(\frac{h^2}{2\pi k_B T} \right)^{1/2}$$

The thermal De-Broglie length

$$p(T) = T \left(\frac{T}{T_o} \right)^{3/2} g_{5/2}(z(T))$$

Where $z(T)$ satisfies the equation

$$\left(\frac{T}{T_o} \right)^{3/2} g_{3/2}(z(T)) = 1$$

The energy of the per particle

$$E(T) = \frac{3}{2} p(T) = \frac{3}{2} T \left(\frac{T}{T_o} \right)^{3/2} g_{5/2}(z(T))$$

if $T > T_c$

$$\left(\frac{T_c}{T_o} \right)^{3/2} g_{3/2}(1) = 1$$

Riemann zeta function

$$z(R) = \sum_{k=1}^{\infty} \frac{1}{k^{\alpha}}$$
$$T(z) = g_{3/2}(z)^{-2/3}$$

Where T is function of fugacity

$$T(z) = g_{3/2}(z)^{-2/3}$$

if $T < T_c$, $z = 1$. Therefore one has

$$E = \frac{3}{2}T \left(\frac{T}{T_o} \right)^{3/2} g_{3/2}(1)$$

Problem: 7.4- Consider a system of N quantum particles of spin zero and mass m on d dimensions subject to a harmonic potential form

$$U(r) = \frac{1}{2}m\omega_o^2 r^2$$

- (a) Give expression of grand canonical function
- (b) Give expression of number N' of particles

Solution

(a)

The grand canonical function

$$E_k = \hbar\omega_o \left(\sum_{k=1}^d k_i + \frac{d}{z} \right)$$

Thus grand canonical function at temperature T

$$\ln z = - \sum_k \ln (1 - e^{-(E_k - U)/k_B T})$$

The sum

$$\begin{aligned}
 N' &= \sum_{k'} \frac{1}{\frac{e^{E_k/k_B T}}{z-1}} \\
 &= \sum_{n=1}^{\infty} \frac{Nd(n)}{\frac{e^{E_k/k_B T}}{z-1}}
 \end{aligned}$$

$Nd(n)$ is a polynomial in n of degree 1, we have

$$\ln z = - \sum_{n=0}^{\infty} Nd(n) \ln(1 - ze^{-kn})$$

Where we have introduced the factuality

$$z = e^{-(U_o - U)/k_B T}$$

(b)

The number of particles in excited state

$$N = \sum_{n=0}^{\infty} \frac{Nd(n)}{s^{kn}/(z-1)}$$

Problem: 7.5- For a semi-conductor without impurities and with an energy gap E_g show

$$U_e = \frac{E_g}{2} + \frac{k_B T}{2} \ln \left(n \frac{Q_k}{n Q_s} \right)$$

Where the subscripts e and h refers to electron and holes.

Solution

In equilibrium

$$\begin{aligned}
 U_e + U_h &= 0 \\
 ne &= nh
 \end{aligned}$$

In the limits of a low density non-interacting gas at high temperature

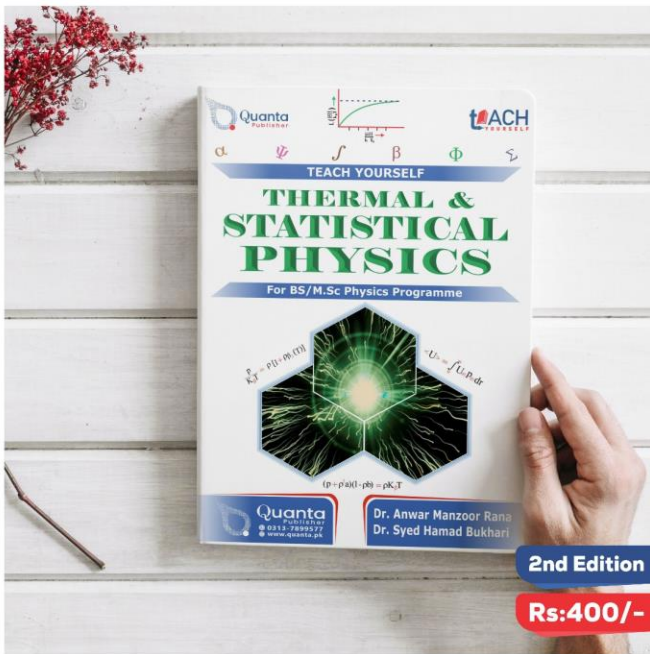
$$U = \Delta + k_B T \ln \left(\frac{n}{n_Q} \right)$$

$$U = E_g + k_B T \ln \left(\frac{n_e}{n_Q} \right)$$

$$nh = n_Q k' e^{U_n/k_B T}$$

$$nh = 2n_Q e^{-U_o/k_B T} = ne$$

$$U_e = \frac{E_g}{2} + \frac{k_B T}{2} \ln \left(n \frac{Q_n}{n_Q} \right)$$



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