Thermodynamics: Classical to Statistical

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Lecture - 37

Advance Problems - 5

Problem 11:

In a system of weakly interacting particles, in equilibrium at temperature T K, each particle has access to two states with energy difference $\varepsilon_2 - \varepsilon_1 = 0.1$ eV. At what temperature will one third of particles be found to have energy ε_2?

Rework the above problem by considering the ε_2 state is doubly degenerate.

Solution:

We know,

$$\frac{n_2}{n_1} = e^{-\beta(\epsilon_2 - \epsilon_1)}$$

where n_1 is the number of particles in the energy state ε_1 and n_2 is the number of particles in the energy state ε_2.

Suppose 'N' is the total number of particles. Thus,

$$n_1 + n_2 = N$$

The number of particles in the energy state ε_2 is $n_2 = \frac{N}{3}$

The number of particles in the energy state ε_1 is $n_1 = \frac{2N}{3}$

Thus,

$$\frac{n_2}{n_1} = \frac{\frac{N}{3}}{\frac{2N}{3}} = \frac{1}{2}$$

So,

$$\frac{1}{2} = e^{-\beta(\epsilon_2 - \epsilon_1)}$$

Or, $$-ln2 = -\beta(\epsilon_2 - \epsilon_1)$$

Or, $$\beta = \frac{ln2}{\epsilon_2 - \epsilon_1}$$

$$\text{Or,} \quad \frac{1}{k_B T} = \frac{ln2}{\epsilon_2 - \epsilon_1}$$

$$\text{Or,} \quad T = \frac{\epsilon_2 - \epsilon_1}{k_B ln2} = \frac{0.1 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times ln2}$$

$$\text{Or,} \quad T = 1672.69\, K$$

When the excited state is doubly degenerate, then we can write,

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\beta(\epsilon_2 - \epsilon_1)}$$

where g_1 = degeneracy of the energy state ε_1 = 1

g_2 = degeneracy of the energy state ε_2 = 2

We know,

$$\frac{1}{2} = 2e^{-\beta(\epsilon_2 - \epsilon_1)}$$

$$\text{Or,} \quad -ln2 = \ln 2 - \beta(\epsilon_2 - \epsilon_1)$$

$$\text{Or,} \quad \beta = \frac{2ln2}{\epsilon_2 - \epsilon_1}$$

$$\text{Or,} \quad \frac{1}{k_B T} = \frac{2ln2}{\epsilon_2 - \epsilon_1}$$

$$\text{Or,} \quad T = \frac{\epsilon_2 - \epsilon_1}{2k_B ln2} = \frac{1672.69}{2}$$

$$\text{Or,} \quad T = 836.35\, K$$

Hence when the degeneracy of the excited state is 2, we required half of the temperature compared to the non-degenerate case.

Problem 12:

Molecular hydrogen is usually found in two forms namely, ortho hydrogen and para-hydrogen.

a) After reaching equilibrium at high temperature, what fraction of molecular hydrogen is para-hydrogen? (Assuming that each variety of hydrogen is mostly in its lowest energy state.)
b) At low-temperatures, ortho hydrogen converts mostly to para-hydrogen. Explain why the energy released by each converting molecule is much larger than the energy change due to the nuclear spin flip.

Solution:

a) Molecular partition function of para-hydrogen is given by

$$q_{para} = \sum_{J=0,2,4,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

The molecular partition function for ortho hydrogen is

$$q_{ortho} = \sum_{J=1,3,5,..}^{\infty} (2J+1) e^{-J(J+1)\frac{\theta_{rot}}{T}}$$

θ_{rot} = the rotational temperature = $\frac{h^2}{8\pi^2 I k_B}$

h = the Plank's constant

I = the moment of energy of the molecule

k_B = the Boltzmann constant.

For high-temperature, $q_{para} = q_{ortho}$,

$$\frac{n_{para}}{n_{ortho}} = \frac{1}{4}$$

According to the condition given in the problem (temperature is not too high), only states J = 0 and 1 exists.

The fraction of para-hydrogen is,

$$\frac{n_{para}}{n_{H_2}} = \frac{Z_{para}}{Z_{H_2}}$$

where $Z_{H_2} = S(2S+1)Z_{para} + (S+1)(2S+1)Z_{ortho}$

and n_{H_2} is the total number of hydrogen molecule.

$$\frac{n_{para}}{n_{H_2}} = \frac{Z_{para}}{Z_{H_2}} = \frac{1}{1 + 3e^{-\frac{2\theta_{rot}}{T}}}$$

b) When T << θ_{rot}, ortho hydrogen changes into para-hydrogen. The energy corresponding to the change in nuclear spin orientation is the coupling energy of the magnetic dipoles of the nuclei and the electrons.

$$\Delta E_{SJ} \sim 10^8 \text{ Hz}$$

Since, the rotational states are related to the nuclear spin states, the rotational states also change. The corresponding energy change being,

$$\Delta E_R = \frac{h^2}{8\pi^2 I} \approx 10^{11} Hz$$

When ortho hydrogen converts to para-hydrogen, the total energy change is

$$\Delta E = \Delta E_R + \Delta E_{SJ} \approx \Delta E_R$$

Thus, the released energy is much greater than ΔE_{SJ}.

Problem 13:

Consider a single magnetic dipole in equilibrium with a heat bath. It has two micro states, namely, up spin and down spin having energies -mH and +mH respectively. What is the average energy of the dipole?

Solution:

The partition function q is

$$q = \sum_{i=1}^{2} e^{-\beta\epsilon_i}$$

$$\text{Or,} \quad q = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}$$

$\varepsilon_1 = -mH$ and $\varepsilon_2 = +mH$

$$q = e^{\beta mH} + e^{-\beta mH}$$

$$lnq = \ln(e^{\beta mH} + e^{-\beta mH})$$

The average energy is

$$< \varepsilon > = -\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

$$\text{Or,} \quad < \varepsilon > = \frac{mH(e^{-\beta mH} - e^{\beta mH})}{(e^{\beta mH} + e^{-\beta mH})}$$

Problem 14:

The fermi energy in silver is 5.51 eV.

i. What is the average energy of free electrons in silver and 0 K temperature?
ii. At what temperature a classical free particle (e.g., an ideal gas molecule) will have this kinetic energy?

Solution:

i. At 0 K temperature, the average energy of an electron in an electron gas is given by

$$\overline{E_0} = \frac{3}{5} \times E_F = \frac{3}{5} \times 5.51eV$$

$$\text{or,} \quad \overline{E_0} = 3.306eV$$

ii. The kinetic energy of a classical particle at T K temperature is $\frac{3}{2}k_BT$. Therefore,

$$\frac{3}{2}k_BT = \frac{3}{5}E_F$$

$$\text{Or,} \quad T = \frac{3}{5} \times \frac{E_F}{k_B}$$

$$\text{Or,} \quad T = \frac{3}{5} \times \frac{5.51 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}}$$

$$\text{Or,} \quad T = 2.55 \times 10^4\ K$$

Problem 15:

(a) You are given a system of two identical particles which may occupy any of the three energy levels, $\epsilon_n = n\epsilon$, where, n = 0, 1, 2, ….

The lowest energy state, $\varepsilon_\circ = 0$, is doubly degenerated.

The system is in thermal equilibrium at temperature T K. For each of the following cases, determine the partition function and the energy and carefully enumerate in the configurations.

i. The particles obey Fermi statistics.
ii. The particles obey Bose statistics.
iii. The now distinguishable particles obey Boltzmann statistics.

(b) Discuss the conditions under which fermions or Bosons may be treated as Boltzmann particles.

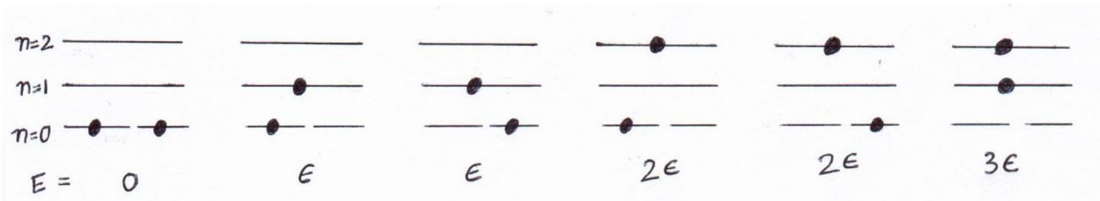
Solution:

(a) Considering the canonical ensemble, the partition function q is

$$q = \sum_n g_n e^{-\beta\epsilon_n}$$

Where g_n is the degeneracy of the energy level n.

i. When the particles obey Fermi statistics, we get the following distributions,



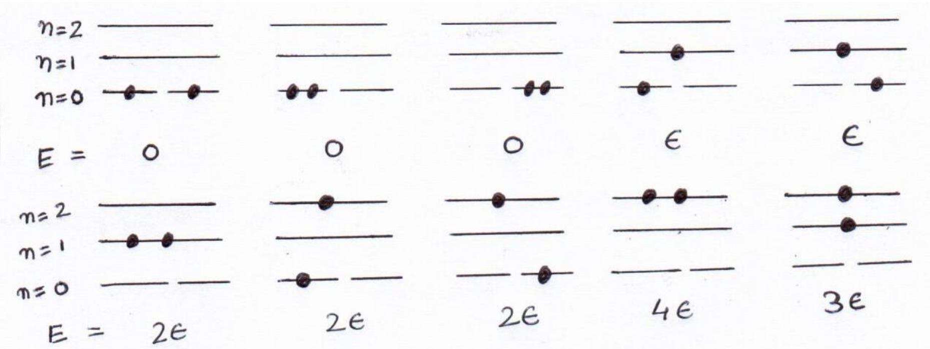
$$q = 1e^{-\beta 0} + 2e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

Or, $$q = 1 + 2e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$$

$$< \varepsilon > = -\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

$$< \epsilon > = \frac{\epsilon}{q} e^{-\beta\epsilon}(2 + 4e^{-\beta\epsilon} + 3e^{-2\beta\epsilon})$$

ii. When the particles are following Bose statistics, the particles are indistinguishable but there is no restriction in a number of particles in a given state, so we get the following distributions,



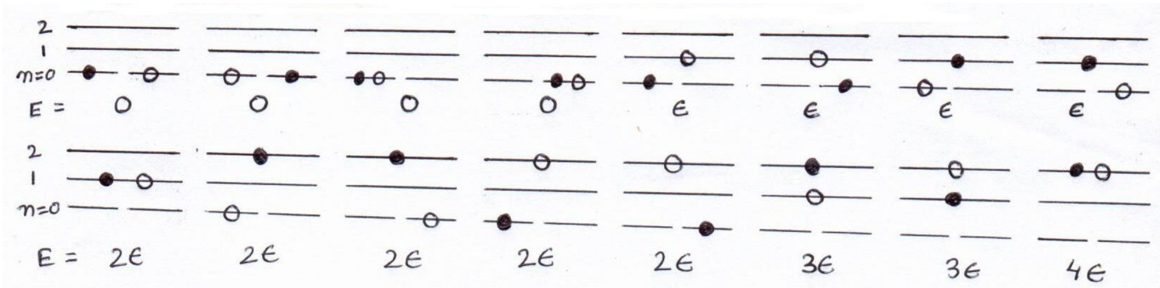
The partition function q,

$$q = 3 + 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

The average energy is

$$< \epsilon > = \frac{\epsilon}{q} e^{-\beta\epsilon}(2 + 6e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + 4e^{-3\beta\epsilon})$$

iii. When the particles obey Boltzmann statistics particles, they are distinguishable and there is no restriction in number of particles in a given state, so the following 16 distributions are possible.



The partition function q is

$$q = 4 + 4e^{-\beta\epsilon} + 5e^{-2\beta\epsilon} + 2e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

From there we get average energy,

$$< \epsilon > = \frac{2\epsilon}{q} e^{-\beta\epsilon}(2 + 5e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + 2e^{-3\beta\epsilon})$$

(b) Discussed in the lecture.

Ergodic Hypothesis

It states that the time average equals the ensemble average.

$$< A >_{ensemble} = < A >_{time}$$

where A is any macroscopic variable.

The $< A >_{time}$ can be calcuated by

$$< A >_{time} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(t) dt$$

The basic idea is that if one allows the system to evolve in time indefinitely, that system will eventually pass through all possible states.