Thermodynamics: Classical to Statistical

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Lecture - 36

Advance Problems - 4

Problem 5:

The energy level of an oscillator with frequency ν is given by,

$$\varepsilon = \frac{1}{2}h\nu,\ \frac{3}{2}h\nu,\ \ldots\ldots\ldots,\ \left(\mathrm{n}+\frac{1}{2}\right)h\nu$$

When a system consisting of 'N' independent oscillators has the total energy,

$$E = \frac{1}{2}Nh\nu + Mh\nu$$

where M is an integer.

i. Find the thermodynamic weight w_M

ii. Determine the relation between the temperature of the system and energy E.

Solution:

i. If the quantum number of the i-th oscillator is denoted by n_i and $E = \frac{1}{2}Nh\nu + Mh\nu$

implies that $n_1 + n_2 + n_3 + \ldots\ldots\ldots + n_N = M$.

Therefore, it is assumed that the thermodynamic weight of a macroscopic state with the total energy E is equal to the number of ways of distributing 'M' white balls among 'N' labeled boxes.

$$w_M = \frac{(M+N-1)!}{M!(N-1)!}$$

ii. $S = k_B \ln w_M$

Substituting the value of w_M and using Stirling's approximation under the assumption that $N \gg 1$ and $M \gg 1$, we can write

$$S = k_B\left\{(M+N)\ln(M+N) - M\ln M - N\ln N\right\}$$

Now the statistical temperature T(E) is expressed by

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial M}\frac{\partial M}{\partial E}$$

Or, $$\frac{1}{T} = k_B \ln\left(\frac{M+N}{M}\right)\frac{\partial M}{\partial E}$$

Or, $$\frac{1}{T} = \frac{k_B}{h\nu}\ln\left(\frac{M+\frac{1}{2}N+\frac{1}{2}N}{M+\frac{1}{2}N-\frac{1}{2}N}\right)$$

Or, $$\frac{1}{T} = \frac{k_B}{h\nu}\ln\left(\frac{\frac{E}{N}+\frac{1}{2}h\nu}{\frac{E}{N}-\frac{1}{2}h\nu}\right)$$

or, inversely, we can write

$$\left(\frac{\frac{E}{N}+\frac{1}{2}h\nu}{\frac{E}{N}-\frac{1}{2}h\nu}\right) = e^{\frac{h\nu}{k_B T}}$$

Solving this for energy, we get

$$E = N\left\{\frac{1}{2}h\nu + \frac{h\nu}{e^{\frac{h\nu}{k_B T}}-1}\right\}$$

Problem 6:

There are 1000 molecules of an ideal gas in a box of 1 L volume. Assuming that the particles do not preferentially occupy any region, find the probability of finding the particles in a particular region of volume 100 cm^3. For what value of 'n' where n is the number of particles is this probability maximum?

Solution:

The probability of finding a molecule in a volume of 100 cm^3 $= \frac{1}{10}$

since the volume of the box = 1 L.

If 'n' numbers of particles are to be there, the probability = $\frac{1}{10}^{n}$

We had 1000 particles out of which 'n' particles are present in a volume of 100 cm^3.

The remaining (1000-n) number of particles must be in the residual volume of 900 cm^3 having a probability of $\frac{9}{10}^{1000-n}$.

Hence, the probability of finding a particular set of 'n' molecules in 100 cm^3 volume is 1 $\left(\frac{1}{10}\right)^n \left(\frac{9}{10}\right)^{1000-n}$.

Since, we can choose 'n' molecules out of 1000 molecules in $^{1000}C_n$ different ways, the probability of finding the particles in a particular region of volume 100 centimeter cm^3 is

$$P(n) = C_n^{1000} \left(\frac{1}{10}\right)^n \left(\frac{9}{10}\right)^{1000-n}$$

Now, if you take the log of both sides we get,

$$\ln P(n) = ln1000! - ln\, n! - \ln(1000-n)\,! - nln10 + (1000-n)ln\frac{9}{10}$$

Using Stirling's approximation,

$$\ln P(n) = ln1000! - nln\, n + n - (1000-n)\ln(1000-n) + (1000-n) - nln10 + (1000-n)ln\frac{9}{10}$$

Differentiating the above expression with respect to n,

$$\frac{dlnP(n)}{dn} = -ln\, n + 1 + \ln(1000-n) + 1 - 1 - ln10 - ln\frac{9}{10}$$

Or, $$\frac{dlnP(n)}{dn} = -ln\, n + \ln(1000-n) - ln9$$

Or, $$\frac{dlnP(n)}{dn} = ln\frac{1000-n}{9n}$$

For maximum probability, we can write,

$$ln\frac{1000-n}{9n} = 0 = ln1$$

Or, $$\frac{1000-n}{9n} = 1$$

Or, $$n = 100$$

Problem 7:

The three lowest energy levels of a certain molecule are $E_1 = 0$, $E_2 = \varepsilon$ and $E_3 = 10\varepsilon$. Show that at sufficiently low temperature only E_1 and E_2 are populated. Find the average energy, E, of the molecule at temperature T and the contributions of three levels to molar specific heat $\overline{C_v}$. Plot $\overline{C_v}$ versus absolute temperature 'T'.

Solution:

Let 'N' be the number of particles in the system.

$$N = N_1 + N_2 + N_3$$

considering that there are only three energy levels of a molecule, E_1, E_2 and E_3 are available. N_1, N_2 and N_3 are the number of particles in energy levels E_1, E_2 and E_3 respectively.

$$\frac{N_1}{N} = \frac{e^{-\beta E_1}}{Q} \quad \text{and} \quad \frac{N_2}{N} = \frac{e^{-\beta E_2}}{Q}.$$

So,

$$\frac{N_2}{N_1} = e^{-\beta\varepsilon} = e^{-\frac{\varepsilon}{k_B T}}$$

Or, $$N_2 = N_1 e^{-\frac{\varepsilon}{k_B T}}$$

Similarly,

$$N_3 = N_1 e^{-\frac{10\varepsilon}{k_B T}}$$

Now,

$$N = N_1 + N_2 + N_3$$

Or, $$N_1 + N_1 e^{-\frac{\varepsilon}{k_B T}} + N_1 e^{-\frac{10\varepsilon}{k_B T}} = N$$

Or, $$N_1 = \frac{N}{1 + e^{-\frac{\varepsilon}{k_B T}} + e^{-\frac{10\varepsilon}{k_B T}}}$$

So,

$$N_3 = \frac{N e^{-\frac{10\varepsilon}{k_B T}}}{1 + e^{-\frac{\varepsilon}{k_B T}} + e^{-\frac{10\varepsilon}{k_B T}}}$$

Or, $$N_3 = \frac{N}{e^{\frac{10\varepsilon}{k_B T}} + e^{\frac{9\varepsilon}{k_B T}} + 1}$$

When T is very low, then $N_3 \approx 0$.

Hence only the energy levels E_1 and E_2 are populated at a low critical temperature T_C.

T_C satisfies the equation

$$\frac{N}{e^{\frac{10\varepsilon}{k_B T}} + e^{\frac{9\varepsilon}{k_B T}} + 1} = 1$$

At critical temperature T_C there is only one particle in level 3 and below T_C there is practically no particle.

If N >> 1 then,

$$N \approx e^{\frac{10\varepsilon}{k_B T_C}}$$

$$T_C = \frac{10\varepsilon}{k_B \ln N}$$

The average energy, <E> average is

$$< E > = \frac{\varepsilon(e^{-\frac{\varepsilon}{k_B T}} + 10e^{-\frac{10\varepsilon}{k_B T}})}{1 + e^{-\frac{\varepsilon}{k_B T}} + e^{-\frac{10\varepsilon}{k_B T}}}$$

The molar specific heat $\overline{C_v}$ is

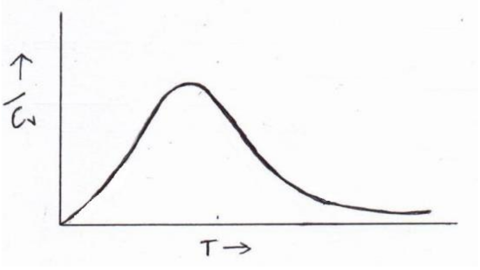
$$\overline{C_v} = N_A \left(\frac{\partial E}{\partial T}\right)_V$$

$$\bar{C}_V = \frac{R\varepsilon^2(e^{-\frac{\varepsilon}{k_B T}} + 100e^{-\frac{10\varepsilon}{k_B T}} + 81e^{-\frac{11\varepsilon}{k_B T}})\beta^2}{\left(1 + e^{-\frac{\varepsilon}{k_B T}} + e^{-\frac{10\varepsilon}{k_B T}}\right)^2}$$

For low temperature when $k_B T \ll \varepsilon$, we get,

$$\bar{C}_V \approx \frac{R\varepsilon^2 e^{-\frac{\varepsilon}{k_B T}}}{(k_B T)^2}$$

The plot $\overline{C_v}$ versus absolute temperature looks like,



Problem 8:

For a monovalent ion, which by definition gives 1 electron, calculate the value of Fermi energy, ε_F. Given, the number density value is 10^{-29} m^{-3}.

Solution:

The Fermi energy ε_F is

$$\varepsilon_F = \frac{\hbar^2}{2m_e}\left(\frac{6\pi^2}{(2S+1)}\frac{N}{V}\right)^{\frac{2}{3}}$$

Plank's constant, h = 6.626×10^{-34} J s

The mass of electron, m_e = 9.1×10^{-31} kg

The number density, $\frac{N}{V}$ = 10^{-29} m^{-3}

The spin of the electron, S = $\frac{1}{2}$, so (2S+1) = 2.

Substituting all these values we get,

$$\varepsilon_F = 2.715 \times 10^{-57} J$$

Problem 9:

Consider a free electron gas at 0 K temperature and show that the de Broglie wavelength associated with an electron is given by

$$\lambda_F = 2\left(\frac{\pi}{3n_{\circ}}\right)^{\frac{1}{3}}$$

where $n_{\circ}$ is the number of electrons per cm^3 of gas.

Solution:

The momentum 'p' of the electron is given by

$$p = \sqrt{2mE_F}$$

We have,

$$\left(E_F\right)_{0K} = \frac{\hbar^2}{2m_e}\left(\frac{6\pi^2}{(2S+1)}\frac{N}{V}\right)^{\frac{2}{3}}$$

(2S+1) = 2

$$\text{Or,} \quad E_F = \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}$$

So, the de Broglie wavelength is

$$\lambda_F = \frac{h}{p} = \frac{h}{\sqrt{2m_e E_F}}$$

$$\text{Or,} \quad \lambda_F = \frac{h}{\sqrt{2m_e \times \frac{h^2}{8m_e}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}}}$$

$$\text{Or,} \quad \lambda_F = \frac{h}{\sqrt{\frac{h^2}{4}\left(\frac{3N}{\pi V}\right)^{\frac{2}{3}}}}$$

$$\text{Or,} \quad \lambda_F = \frac{1}{\frac{1}{2}\left(\frac{3N}{\pi V}\right)^{\frac{1}{3}}}$$

$$\text{Or,} \quad \lambda_F = 2\left(\frac{\pi}{3n_\circ}\right)^{\frac{1}{3}}$$

Problem 10:

A system of two energy levels E_0 and E_1 are populated by ‘N’ particles at temperature ‘T’. The particles populate the energy levels according to the classical distribution law.

i. Derive an expression for the average energy per particle.
ii. Compute the average energy per particle versus the absolute temperature as $T \rightarrow 0$ and $T \rightarrow \infty$.

iii. Derive an expression for the specific heat of the system of 'N' particles.
iv. Compute the specific heats in the limits T goes 0 and T goes to ∞.

Solution:

i. The average energy of the particle is

$$<E> \;= \frac{E_0 e^{-\beta E_0} + E_1 e^{-\beta E_1}}{e^{-\beta E_0} + e^{-\beta E_1}}$$

Assuming $E_1 > E_\circ > 0$ and ΔE is $E_1 - E_\circ$

$$<E> \;= \frac{E_0 + E_1 e^{-\beta \Delta E}}{1 + e^{-\beta \Delta E}}$$

ii. When T → 0 or β → ∞

$$<E> \;= \left(E_0 + E_1 e^{-\beta\Delta E}\right)\left(1 - e^{-\beta\Delta E}\right)$$

Or, $$<E> \;= E_0 + \Delta E e^{-\beta \Delta E}$$

When T → ∞ or β → 0

$$<E> \;\approx \frac{1}{2}\left(E_0 + E_1 - \beta E_1 \Delta E\right)\left(1 + \frac{1}{2}\beta\Delta E\right)$$

Or, $$<E> \;\approx \frac{1}{2}\left(E_0 + E_1\right) - \frac{\beta}{4}\left(\Delta E\right)^2$$

iii. The specific heat (per mole) is

$$\bar{C} = N_A \frac{\partial <E>}{\partial T}$$

Or, $$\bar{C} = N_A \left(\frac{\partial <E>}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

Or, $$\bar{C} = R\left(\frac{\Delta E}{k_B T}\right)^2 \frac{e^{-\frac{\Delta E}{k_B T}}}{\left(1 + e^{-\frac{\Delta E}{k_B T}}\right)^2}$$

iv. When T → 0

$$\bar{C} \approx R\left(\frac{\Delta E}{k_B T}\right)^2 e^{-\frac{\Delta E}{k_B T}}$$

When T → ∞

$$\bar{C} \approx \frac{R}{4}\left(\frac{\Delta E}{k_B T}\right)^2$$