VIVEKANANDA COLLEGE THAKURPUKUR KOLKATA-700063

NAAC ACCREDITED 'A' GRADE

Topic: Further application of Canonical Ensemble
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Energy fluctuation, Equipartition Theorem in Canonical Ensemble

Statistical Mechanics, Arvind Pan

Energy fluctuation

Although different physical condition apply to canonical ensemble and microcanonical ensemble i.e. in Canonical ensemble, a system can have energy anywhere between zero and infinity, but in case of microcanonical ensemble, the energy is restricted to a very narrow range

Is the formalism canonical ensemble be the same as that of microcanonical one as they yield identical thermodynamic results?

Free [illegible]

Canonical Ensemble : Energy can vary between 0 to ∞. (N, V, T) $U = \frac{3}{2} NkT$

Microcanonical Ensemble : " " " " $E - \Delta$ to $E + \Delta$. (N, E, V) $U = \frac{3}{2} NkT$

But both results in same thermodynamic parameters value p, A, E, C_v

That should be the case but how do we assert that mathematically?

$$U = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \Rightarrow \frac{\partial U}{\partial \beta} = \frac{\sum_r -E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} - \frac{1 \times \sum -E_r e^{-\beta E_r} \sum E_r e^{-\beta E_r}}{\left(\sum_r e^{-\beta E_r}\right)^2}$$

$$\frac{\partial U}{\partial \beta} = -\langle E^2 \rangle + \langle E \rangle^2 \Rightarrow -\frac{\partial U}{\partial \beta \left(\frac{1}{kT}\right)} = \langle E^2 \rangle - \langle E \rangle^2$$

$$\therefore \langle E^2 \rangle - \langle E \rangle^2 = kT^2 \frac{\partial U}{\partial T} = kT^2 C_v$$

R.M.S fluctuation in Energy

$$\frac{\langle (\Delta E)^2 \rangle^{1/2}}{E} = \frac{\sqrt{kT^2 C_v}}{E} \propto \frac{1}{N^{1/2}}$$

$C_v \propto N$

$E \propto N$

$$O\left(N^{-1/2}\right)$$

$N \to$ no. of particles in the system $\to$ large RMS fluctuations become very small. Hence a system in canonical ensemble formalism has energy almost nearly equal to most probable energy U.

Equipartition Theorem

Classical theorem also known as the classical Equipartition of energy:

According to it in classical limiting case every canonical variable (generalized position and momentum) entering quadratically or harmonically in a Hamiltonian function(Energy) has a mean thermal energy kT/2. In order to prove that, we are interested in calculating the mean value of the quantity $xi\partial H/\partial xj$ where $xi$and xj are any of 6N phase space coordinates

Now $e^{-\beta H}\left(x_i \frac{\partial H}{\partial x_j}\right) = -\frac{1}{\beta} x_i \frac{\partial}{\partial x_j} e^{-\beta H}$

So

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{-\frac{1}{\beta}\int x_i \frac{\partial}{\partial x_j}(e^{-\beta H})\, d\omega}{\int e^{-\beta H} d\omega}$$

Integrating the numerator over x_j, we have

$$-\frac{1}{\beta} x_i e^{-\beta H}\Big|_{x_j(1)}^{x_j(2)} d\omega_j + \frac{1}{\beta}\int \frac{\partial x_i}{\partial x_j} e^{-\beta H} dx_j \; d\omega_j$$

where $x_j(1)$ & $x_j(2)$ are the extreme values of x_j, so $H(x_i) = \infty$

so $e^{-\beta H} \to 0$ ~~Hence~~ and $d\omega_j$ is the volume $d\omega$ devoid of dx_j

So the numerator can be written as $\frac{1}{\beta}\int \frac{\partial x_i}{\partial x_j} e^{-\beta H} d\omega = \delta_{ij}$ ...

Hence $\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\beta}\delta_{ij} = KT\delta_{ij}$

For $x_i = x_j = p_i \Rightarrow \left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle = \langle p_i \dot{q}_i \rangle = KT$

For $x_i = x_j = q_i \Rightarrow \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = -\langle q_i \dot{p}_i \rangle = KT$

Adding over all degree of freedom for $i = 1$ to $3N$

$$\left\langle \sum_{i=1}^{3N} p_i \frac{\partial H}{\partial p_i} \right\rangle = \langle \sum p_i \dot{q}_i \rangle = 3NKT$$

By using suitable canonical tranformation, Let us take ...
which is quadratic is all 6N coordinates i.e

$$H = \sum_j A_j P_j^2 + \sum_j B_j Q_j^2$$

$\left| \begin{matrix} P_j \\ Q_j \end{matrix} \right\}$ Canon... Tran...

Hence one can see that