PHYS4006: Thermal and Statistical Physics

Lecture Notes
(Part - 1 ; Unit - V)

# Fluctuations in Thermodynamic Quantities

**Dr. Neelabh Srivastava**
(Assistant Professor)
Department of Physics
Mahatma Gandhi Central University
Motihari-845401, Bihar
E-mail: neelabh@mgcub.ac.in

Programme: M.Sc. Physics

Semester: 2nd

- The properties of a system vary with time about the mean equilibrium values. It has been observed that in the neighborhood of a critical point, fluctuations in some thermodynamic quantities e.g. pressure (P), energy (E), entropy (S) and specific heat ($C_V$) are predominant.

- So, far we have assumed that the fluctuations in these thermodynamic quantities are quite small.

- In a system which contains small number of particles in equilibrium with its surroundings, fluctuations are violent.

- So, to represent the thermodynamic quantities of a system more precisely, fluctuations in these quantities should be calculated.

- If energy (E) fluctuations in the system of a canonical ensemble are small, it is equivalent to a microcanonical ensemble.

- If both N and E of the system in a grand canonical ensemble fluctuate negligibly then all the three ensembles are equivalent.

# Mean-square Deviation

- Consider a quantity *n*. Its average value is $\overline{n}$ or $\langle n \rangle$

The deviation δn of the quantity from its average value is defined by –

$$\delta n \equiv n - \overline{n} \quad \text{.............(1)}$$

$$\overline{\delta n} = \overline{n} - \overline{n} = 0 \quad \text{.........(2)}$$

Rough measure of the fluctuations is provided by the *mean-square deviation*

$$\overline{(\delta n)^2} = \overline{\left(n - \overline{n}\right)^2} = \overline{n^2} - 2\overline{n}\,\overline{n} + \left(\overline{n}\right)^2$$

$$\overline{(\delta n)^2} = \overline{n^2} - \left(\bar{n}\right)^2 \quad \text{..........(3)}$$

$\overline{n^2}$ is called the second moment of the distribution. The standard deviation Δn, the root mean square deviation from the mean is defined as -

$$\Delta n = \left[\overline{\left(n - \bar{n}\right)^2}\right]^{1/2} \quad \text{..........(4)}$$

Let $P_i$ be the probability of finding a system in the state $i$ and if $f_i$ is the value of a physical quantity $f$ when the system is in the state $i$ then average value of $f$ is defined by -

$$\overline{f} = \sum_i P_i f_i \quad with \quad \sum_i P_i = 1 \quad .......(5)$$

Then,

$$\overline{f - \overline{f}} = \sum P_i \left( f_i - \overline{f} \right) = \sum P_i f_i - \overline{f} \sum P_i$$

$$\overline{f - \overline{f}} = \overline{f} - \overline{f} = 0 \quad ...........(6)$$

$$\overline{\left( f - \overline{f} \right)^2} = \sum P_i \left( f_i - \overline{f} \right)^2 = \sum P_i f_i^2 - 2\overline{f} \sum P_i f_i + \left( \overline{f} \right)^2 \sum P_i$$

$$\overline{\left( f - \overline{f} \right)^2} = \overline{f^2} - 2\left( \overline{f} \right)^2 + \left( \overline{f} \right)^2 = \overline{f^2} - \left( \overline{f} \right)^2 \quad ..........(7)$$

and

$$\Delta f = \left[ \overline{f^2} - \left( \overline{f} \right)^2 \right]^{1/2} \quad ..........(8)$$

# Fluctuations in Energy

- Consider a ‘closed system’ in thermodynamic equilibrium at a given temperature and is represented by a canonical ensemble.

- Since, in this ensemble, system is in thermal equilibrium with a heat reservoir so fluctuations can not occur in temperature but only in energy when the energy is exchanged between the system and the reservoir.

The canonical partition function is

$$Z = \sum_i \exp(-\beta E_i) \quad \text{.................(9)}$$

$$\overline{E} = \sum_i P_i E_i = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} = \frac{-\partial Z / \partial \beta}{Z} \quad \text{................(10)}$$

$$\overline{E^2} = \frac{\sum_i E_i^2 \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} = \frac{-\partial^2 Z / \partial^2 \beta}{Z} \quad \text{................(11)}$$

$$-\frac{\partial \overline{E}}{\partial \beta} = \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \beta^2}\right) - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \overline{E^2} - \overline{E}^2 = \overline{(\delta E)^2} \quad \text{........(12)}$$

$$C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = \left(\frac{\partial \overline{E}}{\partial \beta}\right)_V \frac{d\beta}{dT} = \left(\frac{\partial \overline{E}}{\partial \beta}\right)_V (-k\beta^2)$$

$$C_V = k\beta^2 \overline{(\delta E)^2}$$

A measure of energy fluctuation is the ratio

$$\frac{\Delta E}{E} = \frac{\left[\overline{(\delta E)^2}\right]^{1/2}}{\overline{E}} = \frac{\left(kT^2 C_V\right)^{1/2}}{\overline{E}} \quad \text{........(13)}$$

As we know that for an ideal gas,

$$\overline{E} = NkT \quad \text{and} \quad C_V = Nk$$

$$\frac{\Delta E}{E} = \frac{1}{\sqrt{N}}$$

## Grand-canonical Ensemble:

Fluctuations in energy can be calculated as done for the case of canonical ensemble. Herein, we study the possibility of concentration fluctuations.

The partition function can be written as –

$$Q(T,V,\mu) = \sum_{N,i} \exp\left[\left(N\mu - E_{N_i}\right)/\theta\right] \quad .........(14)$$

where θ = kT

Average number of particles is given by –

$$\overline{N} = \langle N \rangle = -\left(\frac{\partial \zeta}{\partial \mu}\right)_{V,T}$$

$$\overline{N} = -\left(\frac{\partial \zeta}{\partial \mu}\right)_{V,T} = \theta \frac{\partial}{\partial \mu} \ln Q = \frac{\theta}{Q} \frac{\partial Q}{\partial \mu}$$

$$\overline{N^2} = \frac{\sum_{N,i} N^2 \exp\left[\left(N\mu - E_{N_i}\right)/\theta\right]}{\sum_{N,i} \exp\left[\left(N\mu - E_{N_i}\right)/\theta\right]} = \frac{\theta^2}{Q} \frac{\partial^2 Q}{\partial \mu^2}$$

$$\overline{\left(\delta N\right)^2} = \overline{N^2} - \left(\overline{N}\right)^2 = \theta^2 \left[\frac{1}{Q} \frac{\partial^2 Q}{\partial \mu^2} - \frac{1}{Q^2}\left(\frac{\partial Q}{\partial \mu}\right)^2\right]$$

$$\overline{\left(\delta N\right)^2} = \theta \frac{\partial \overline{N}}{\partial \mu} \qquad \text{..........(15)}$$

But, for an ideal classical gas,

$$\overline{N} = e^{\mu/\theta} \frac{(2\pi m\theta)^{3/2}}{h^3} V \quad \text{.........}(16)$$

$$\frac{\partial \overline{N}}{\partial \mu} = \frac{\overline{N}}{\theta} \quad \text{..........}(17)$$

$$\overline{(\delta N)^2} = \overline{N} = \frac{pV}{kT} \quad \text{..........}(18)$$

Thus, concentration fluctuation is given by -

$$\frac{\Delta N}{N} = \left[ \frac{\overline{(\delta N)^2}}{(\overline{N})^2} \right]^{1/2} = \frac{1}{\overline{N}^{1/2}} \quad \text{..........}(19)$$

# Concentration fluctuations in Quantum Statistics

- The variation of average number of particles in the single particle quantum state, *i* for the system obeying quantum statistics (FD & BE) is given by –

$$\frac{\partial \overline{n_i}}{\partial \mu} = \frac{\partial}{\partial \mu}\left[\frac{1}{\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right) \pm 1}\right] = \frac{1}{\theta}\frac{\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right)}{\left[\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right) \pm 1\right]^2}$$

$$\frac{\partial \overline{n_i}}{\partial \mu} = \frac{1}{\theta}\left[\frac{\left\{\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right) \pm 1\right\} \mp 1}{\left\{\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right) \pm 1\right\}^2}\right]$$

$$\frac{\partial \overline{n_i}}{\partial \mu} = \frac{1}{\theta}\left(\overline{n_i} \mp \overline{n_i}^2\right) = \frac{1}{\theta}\overline{n_i}\left(1 \mp \overline{n_i}\right) \quad \ldots\ldots\ldots\ldots(20)$$

from eq$^n$. (15)

$$\overline{\left(\delta n_i\right)^2} = \theta \frac{\partial \overline{n}}{\partial \mu} = \overline{n_i}(1 \mp \overline{n_i}) \quad \ldots\ldots\ldots\ldots(21)$$

$$\frac{\Delta n_i}{n_i} = \left[\frac{\overline{\left(\delta n_i\right)^2}}{\overline{n_i}^2}\right]^{1/2} = (1 \mp \overline{n_i}^{-1}) \quad \ldots\ldots\ldots\ldots(22)$$

or,

$$\frac{\Delta n_i}{n_i} = \begin{cases} \left(n_i^{-1} - 1\right)^{1/2} & ;(FD) \\ \left(n_i^{-1} + 1\right)^{1/2} & ;(BE) \\ \left(n_i^{-1}\right)^{1/2} & ;(MB) \end{cases} \quad \ldots\ldots\ldots\ldots(23)$$

# One-dimensional Random Walk

- Consider the motion of a drunk sailor who has lost the sense of direction, takes a *random walk in one-dimension*.

- Suppose he takes $N$ steps each of equal length $l$. Let each step be random , i.e. to the forward or backward direction. Each step has a probability of ½ being in either direction.

- Now, we have to find the probability of the drunk person that he is at a distance $x$ from the starting point after such a walk.

Let *P(m, N)* be the probability that the person is at a point m steps away after *N* steps. The probability of any given sequence of *N* steps is $(1/2)^N$.

Hence, $$P(m,N) = \left(\frac{1}{2}\right)^N \times W(m) \quad .........(i)$$

where *W(m)* is the number of distinct sequences that reach m after *N* steps.

To reach at the point m, some set of $n_1 = \frac{1}{2}(N+m)$ steps out of N must be positive and the remaining

$n_2 = \frac{1}{2}(N-m)$ steps must be negative. Therefore, the number of distinct sequences that reach *m* is –

$$W(m) = \frac{N!}{\left[\frac{1}{2}(N+m)!\right]\left[\frac{1}{2}(N-m)!\right]} \quad \text{.........}(ii)$$

For large *N*, the exact form of Stirling's approx. is given by -

$$N! = (2\pi N)^{1/2} N^N e^{-N}$$

$$\ln N! = N \ln N - N - \frac{1}{2}\ln(2\pi N)$$

$$\ln N! = \left(N + \frac{1}{2}\right)\ln N - N + \frac{1}{2}\ln 2\pi \quad \text{.........}(iii)$$

Then,

$$\ln P(m,N) = \left(N+\frac{1}{2}\right)\ln N - \frac{1}{2}(N+m+1)\ln\frac{1}{2}(N+m) - \frac{1}{2}(N-m+1)\ln\frac{1}{2}(N-m) - \frac{1}{2}\ln 2\pi - N\ln 2 \quad \ldots\ldots\ldots(iv)$$

since, m<<N, then $\ln\left(1\pm\frac{m}{N}\right) = \pm\frac{m}{N} - \frac{m^2}{2N^2} \pm \ldots\ldots\ldots \quad \ldots\ldots\ldots.(v)$

using $\ln\frac{1}{2}(N\pm m) = \ln\left(\frac{N}{2}\right) + \ln\left(1\pm\frac{m}{N}\right)$

Therefore, from eq$^n$. (iv)

$$\ln P(m,N) = \left(N+\frac{1}{2}\right)\ln N - \frac{1}{2}(N+m+1)\left(\ln N - \ln 2 + \frac{m}{N} - \frac{m^2}{2N^2}\right) - \frac{1}{2}(N-m+1)\left(\ln N - \ln 2 - \frac{m}{N} - \frac{m^2}{2N^2}\right) - \frac{1}{2}\ln 2\pi - N\ln 2$$

$$\ln P(m,N) \approx -\frac{1}{2}\ln N + \ln 2 - \frac{1}{2}\ln 2\pi - \frac{m^2}{2N^2}$$

or,

$$P(m,N) \approx \left(\frac{2}{\pi N}\right)^{1/2} \exp\left(-\frac{m^2}{2N}\right) \quad .........(vi)$$

as $x=ml$ and $m=n_1-n_2=n_1-(N-n_1)=2n_1-N$

So, the probability that the sailor is between $x$ and $(x+dx)$ after N steps is –

$$P(x,N)\,dx = P(m,N)\,dm = P(m,N)\frac{dx}{2l} \quad ...........(vii)$$

Here, $dx=2ldm$ as $m$ can take integral values separated by $\Delta m=2$.

Hence, the probability that a person is at a distance $x$ after $N$ steps is –

$$P(x,N)=\left(2\pi l^2 N\right)^{-1/2}\exp\left(\frac{-x^2}{2Nl^2}\right) \quad \text{..........}(viii)$$

This is the *normal* or *Gaussian distribution* which is of the form

$$P(x)=\left(2\pi\right)^{-1/2}\gamma^{-1}\exp\left(\frac{-x^2}{2\gamma^2}\right), \quad \int_{-\infty}^{+\infty}P(x)dx=1 \quad \text{..........}(ix)$$

Let us assume that the sailor takes $N=nt$ steps in time $t$. Then, the probability of the sailor being in the interval $dx$ at $x$ after time $t$ is –

$$P(x)\,dx = \left(2\pi l^2 nt\right)^{-1/2} \exp\left(\frac{-x^2}{2ntl^2}\right) dx \quad ..........(x)$$

The mean square distance travelled is given by the mean square fluctuation -

$$\overline{(\delta x)^2} = \overline{x^2} = \int_{-\infty}^{+\infty} x^2 P(x)\,dx$$

$$\overline{x^2} = \int_{-\infty}^{+\infty} x^2 \left(2\pi l^2 nt\right)^{-1/2} \exp\left(\frac{-x^2}{2l^2 nt}\right) dx = l^2 nt \quad ...........(xi)$$

Thus, a random walk is what particles execute when they diffuse and the particle diffusion coefficient (D) defined by –

$$D = \frac{l^2}{2\tau}$$

where τ is the time taken for each step then $t=\tau N$

Therefore, the probability that the sailor will be within $dx$ at $x$ at time $t$ if he was at $x=0$ at $t=0$ is -

$$P(0,0;x,t)\,dx = \left(4\pi Dt\right)^{-1/2} \exp\left(\frac{-x^2}{4Dt}\right) dx \quad \text{..........}(xii)$$

# References: Further Readings


1. *Statistical Mechanics* by R.K. Pathria
2. *Elementary Statistical Mechanics* by Gupta & Kumar
3. *Statistical Mechanics* by K. Huang
4. *Statistical Mechanics* by B.K. Agrawal and M. Eisner

# Thank You

**For any questions/doubts/suggestions and submission of assignment**
**write at E-mail: neelabh@mgcub.ac.in**