Fluctuations in Thermodynamic Quantities

PHYS4006: Thermal and Statistical Physics

Lecture Notes
(Part - 1 ; Unit - V)

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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\textsubscript{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 \( \bar{n} \) or \( \langle n \rangle \)

The deviation \( \delta n \) of the quantity from its average value is defined by –

\[
\delta n = n - \bar{n} \quad \text{...............(1)}
\]

\[
\bar{\delta n} = \bar{n} - \bar{n} = 0 \quad \text{.........(2)}
\]

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

\[
(\delta n)^2 = \left( n - \bar{n} \right)^2 = n^2 - 2\bar{n}n \left( \bar{n} \right)^2
\]
The standard deviation $\Delta n$, the root mean square deviation from the mean is defined as -

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

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 -
\[ \bar{f} = \sum_i P_i f_i \quad \text{with} \quad \sum_i P_i = 1 \quad \text{.......(5)} \]

Then,
\[ f - \bar{f} = \sum_i P_i (f_i - \bar{f}) = \sum_i P_i f_i - \bar{f} \sum_i P_i \]
\[ f - \bar{f} = \bar{f} - f = 0 \quad \text{.............(6)} \]

\[ (f - \bar{f})^2 = \sum_i P_i (f_i - \bar{f})^2 = \sum_i P_i f_i^2 - 2 \bar{f} \sum_i P_i f_i + (\bar{f})^2 \sum_i P_i \]
\[ (f - \bar{f})^2 = f^2 - 2(\bar{f})^2 + (\bar{f})^2 = f^2 - (\bar{f})^2 \quad \text{.............(7)} \]

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

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

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

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

\[ -\frac{\partial \overline{E}}{\partial \beta} = \frac{1}{Z} \left( \frac{\partial^2 Z}{\partial \beta^2} \right) - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 = \overline{E}^2 - \overline{E}^2 = (\delta E)^2 \quad \text{........}(12) \]
A measure of energy fluctuation is the ratio

\[
\frac{\Delta E}{E} = \left[ \left( \delta E \right)^2 \right]^{1/2} = \left( kT^2 C_V \right)^{1/2} \\
\]

As we know that for an ideal gas,

\[
\bar{E} = NkT \quad \text{and} \quad C_V = Nk
\]
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

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

where \( \theta = kT \)

Average number of particles is given by

\[ \overline{N} = \langle N \rangle = -\left( \frac{\partial \xi}{\partial \mu} \right)_{V,T} \]
\[
\overline{N} = -\left( \frac{\partial \zeta}{\partial \mu} \right)_{v,T} = \theta \frac{\partial}{\partial \mu} \ln Q = \frac{\theta}{Q} \frac{\partial Q}{\partial \mu}
\]

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

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

\[
\overline{(\delta N)^2} = \theta \frac{\partial \overline{N}}{\partial \mu} \quad \text{...........(15)}
\]
But, for an ideal classical gas,

$$\bar{N} = e^{\mu/\theta} \left( \frac{2\pi m \theta}{h^3} \right)^{3/2} V \quad \ldots \ldots (16)$$

$$\frac{\partial \bar{N}}{\partial \mu} = \frac{\bar{N}}{\theta} \quad \ldots \ldots (17)$$

$$\left( \delta N \right)^2 = \bar{N} = \frac{pV}{kT} \quad \ldots \ldots (18)$$

Thus, concentration fluctuation is given by -

$$\frac{\Delta N}{N} = \left[ \frac{\left( \delta N \right)^2}{\left( \bar{N} \right)^2} \right]^{1/2} = \frac{1}{\bar{N}^{1/2}} \quad \ldots \ldots (19)$$
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 –

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

\[
\frac{\partial n_i}{\partial \mu} = \frac{1}{\theta} \left[ \frac{\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right) \pm 1}{\left\{\exp\left(\frac{\varepsilon_i - \mu}{\theta}\right) \pm 1\right\}^2} \right]
\]
\[ \frac{\partial \bar{n}_i}{\partial \mu} = \frac{1}{\theta} \left( \bar{n}_i + \bar{n}_i^2 \right) = \frac{1}{\theta} \bar{n}_i \left( 1 + \bar{n}_i \right) \quad \text{...........(20)} \]

from eqn. (15)

\[ \left( \delta n_i \right)^2 = \theta \frac{\partial \bar{n}_i}{\partial \mu} = \bar{n}_i \left( 1 + \bar{n}_i \right) \quad \text{............(21)} \]

\[ \frac{\Delta n_i}{n_i} = \left[ \frac{\left( \delta n_i \right)^2}{\bar{n}_i^2} \right]^{1/2} = \left( 1 + \bar{n}_i^{-1} \right) \quad \text{............(22)} \]

or,

\[ \frac{\Delta n_i}{n_i} = \begin{cases} \left( n_i^{-1} - 1 \right)^{1/2} & ; (FD) \\ \left( n_i^{-1} + 1 \right)^{1/2} & ; (BE) \\ \left( n_i^{-1} \right)^{1/2} & ; (MB) \end{cases} \quad \text{.............(23)} \]
One-dimensional Random Walk

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

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

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

\[ N! = \left(2\pi N\right)^{1/2} N^N e^{-N} \]

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

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

\[
\ln P(m, N) = \left( N + \frac{1}{2} \right) \ln N - \frac{1}{2} (N + m + 1) \ln \frac{1}{2} (N + m) - \frac{1}{2} (N - m + 1) \ln \frac{1}{2} (N - m) - \frac{1}{2} \ln 2\pi - N \ln 2 \quad \text{.........(iv)}
\]

since, \( m \ll N \), then \( \ln \left( 1 \pm \frac{m}{N} \right) = \pm \frac{m}{N} - \frac{m^2}{2N^2} \pm \text{.........} \text{.........}(v) \)

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

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 –

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

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 –

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

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

\[
\langle \delta x \rangle^2 = \bar{x}^2 = \int_{-\infty}^{+\infty} x^2 P(x) \, dx
\]

\[
\bar{x}^2 = \int_{-\infty}^{+\infty} x^2 \left(2\pi l^2 nt\right)^{-1/2} \exp\left(-\frac{x^2}{2l^2nt}\right) \, dx = l^2nt \] ............(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 \( \tau \) 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 -

\[
P(0,0; x, t) \, dx = \left(4\pi Dt\right)^{-1/2} \exp\left(-\frac{x^2}{4Dt}\right) \, dx \quad ............(xii)
\]
References: Further Readings

1. *Statistical Mechanics* by R.K. Pathria

2. *Elementary Statistical Mechanics* by Gupta & Kumar

3. *Statistical Mechanics* by K. Huang

For any questions/doubts/suggestions and submission of assignment
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