LECTURE - I

LECTURE - II

Topics:- ① Mathematical modelling
② Classical mechanics
③ Thermodynamics
④ Statistical Mechanics
⑤ Quantum Mechanics

Reference books:- 1.) Concepts of Modern Physics - Arthur Baser
2.) Feynmann Lectures on Physics
3.) Physical Chemistry - Atkins
4.) Fundamentals of Statistical and thermal Physics - F. Reif
5.) Classical Mechanics - Goldstein
6.) Mechanics - LD Landau & Lifschitz
7.) Quantam Chemistry - I.N. Levine
8.) Quantum mechanics - G.

Grading :- Mid I - 20%
Mid II - 20%
End sem - 40%
Assignments & Quizzes - 20%

$\frac{N!}{N}$ $^N c_{n_1}$ $\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!$

LECTURE-III

Diffusion or Brownian Motion

The model we use is random walk.

$\Rightarrow$ One-Dimensional Random Walk

→ Axioms:-

1) It is one dimensional
2) Particle starts from $x=0$.
3) Each step ~~he/she takes~~ it takes is of equal length (l).
4) The direction of each step is completely independent of the preceding step (i.e it is random).
5) At each time, the probability of a step to be to the right is p, while the probability for step to be to the left is

→ Question:- After N ~~seconds~~ steps, what is the probability of it being at some x?

→ Analysis

n_1 - number of steps to the right

n_2 - number of step to the left

$\therefore n_1 + n_2 = N$

Taking l as a unit,

Net Displacement $= m = (n_1 - n_2)$

$n_1 = \frac{N+m}{2}, n_2 = \frac{N-m}{2}$

We need to find the probability of taking n_1 steps to the right, out of N steps. ($W_{0N}(n_1)$)

Simple cases:-

$N=3, n_1 = 2, n_2 = 1$

$\therefore \rightarrow\rightarrow\leftarrow, \rightarrow\leftarrow\rightarrow, \leftarrow\rightarrow\rightarrow \Rightarrow$ 3 possibilities

$x \rightarrow$ number of experiments.

$v = \sqrt{\frac{3RT}{2m}} = \sqrt{\frac{\gamma RT}{n}} \quad \sqrt{\frac{3X}{2} \times 10}$ $\quad p^{n_1} q^{(N-n_1)} \quad \frac{N!}{N!} \left(\frac{1}{2}\right)^{N/2}$

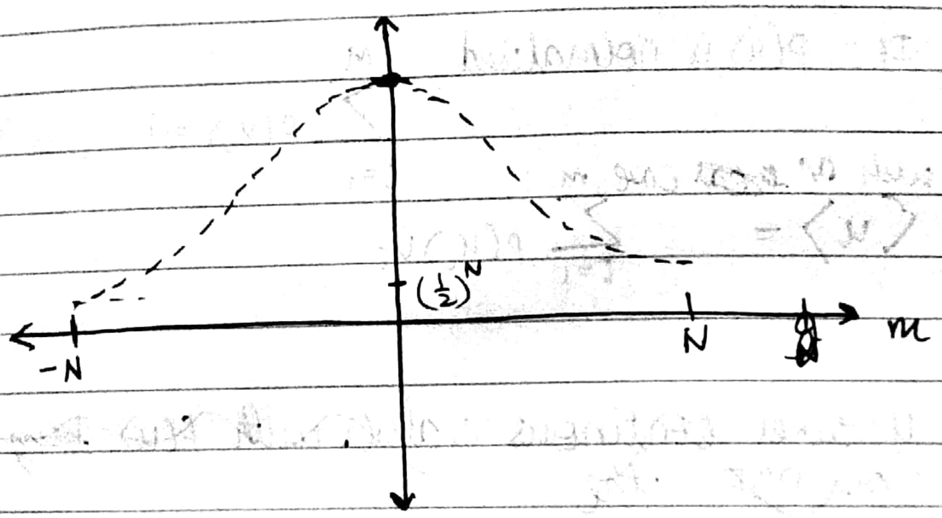
In general

$$W_N(n_1) = \frac{N!}{n_1!\, n_2!} \cdot p^{n_1} \cdot q^{n_2}$$

$\therefore$ Probability for net displacement to be at m after N steps, is

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} \cdot p^{(N+m)/2}\, q^{((N-m)/2)}$$

For unbiased random walk, $p = q = \frac{1}{2}$



→ Statistics :-

we find $\langle n_1 \rangle$

$\langle n_1 \rangle$ – mean value of n_1

$\langle n_1 - \langle n_1 \rangle \rangle$ – mean deviation in n_1 (average of deviation)

$\langle (n_1 - \langle n_1 \rangle)^2 \rangle$ – fluctuation or second moment (average of deviation squared) or mean-squared deviation

$\langle m \rangle$, $\langle m - \langle m \rangle \rangle$, $\langle (m - \langle m \rangle)^2 \rangle$

General statistics :-

If u is a variable that can take M discrete values $\{u_1, u_2, \ldots, u_M\}$ with respective probabilities $p(u_1), p(u_2), \ldots, p(u_M)$

Then,
$$\langle u \rangle = \frac{\sum_{i=1}^{M} p(u_i) u_i}{\sum_{i=1}^{M} p(u_i)}$$

If $p(u)$ is normalised, $\sum_{i=1}^{M} p(u_i) = 1$

$\therefore$ In such a ~~case~~ case,
$$\langle u \rangle = \sum_{i=1}^{M} p(u_i) u_i$$

~~If u takes continous values with $f(u)$ being probability being the PDF, the~~

If $f(u)$ is any function of u, then
$$\langle f(u) \rangle = \frac{\sum_{i=1}^{M} p(u_i) \cdot f(u_i)}{\sum_{i=1}^{M} p(u_i)}$$

If $\Delta u = u - \langle u \rangle$, i.e. Δu is deviation, then
$$\langle \Delta u \rangle = \langle u - \langle u \rangle \rangle = \langle u \rangle - \langle u \rangle = 0$$

$$\langle (\Delta u)^2 \rangle = \langle (u - \langle u \rangle)^2 \rangle$$

$$= \langle u^2 + (\langle u \rangle)^2 - 2u\langle u \rangle \rangle$$

$$= \langle u^2 \rangle + \langle (\langle u \rangle)^2 \rangle - \langle 2u\langle u \rangle \rangle$$

$$= \langle u^2 \rangle + (\langle u \rangle)^2 - 2(\langle u \rangle)^2$$

$$\cancel{= \langle u^2 \rangle - (\langle u \rangle)^2}$$

$$\langle (\Delta u)^2 \rangle = \langle u^2 \rangle - (\langle u \rangle)^2$$

Note that

$$\langle (\Delta u)^2 \rangle \geq 0 \Rightarrow \langle u^2 \rangle \geq (\langle u \rangle)^2$$

n^{th} moment of the Probability Distribution :-

$$\langle (\Delta u)^n \rangle = \langle (u - \langle u \rangle)^n \rangle$$

For our random walker,

$$\langle n_1 \rangle = \sum_{n_1=0}^{N} W_N(n_1) \cdot n_1$$

$$= \sum_{n_1=0}^{N} \left(\frac{N!}{(n_1!)(n_2!)} \cdot p^{n_1} \cdot q^{n_2} \right) \cdot n_1$$

$$= \sum_{n_1=0}^{N} \left(\frac{N!}{n_1!\,(N-n_1)!} \cdot p^{n_1} q^{N-n_1} \right) n_1$$

$\sum_{n=0}^{N} {}^{N}C_{n_1} \, p^{n_1} q^{N-n_1} = (p+q)^N$

$\cancel{f'(p) = \sum_{n_1=0}^{N} {}^{N}C_{n_1} p^{n_1-1} q^{N-n_1}}$

$\langle n_1 \rangle = pN(p+q)^{N-1}$

Note that

$$p \frac{\partial (p^{n_1})}{\partial p} = n_1 p^{n_1}$$

$$\therefore \langle n_1 \rangle = \sum_{n_1=0}^{N} \frac{N!}{n_1!(N-n_1)!} \, q^{N-n_1} \, p \frac{\partial (p^{n_1})}{\partial p}$$

$$\Rightarrow \langle n_1 \rangle = p \frac{\partial}{\partial p} \left[\sum_{n_1=0}^{N} \frac{N! \, q^{N-n_1} p^{n_1}}{n_1! (N-n_1)!} \right]$$

$$= p \frac{\partial}{\partial p} \left[(p+q)^N \right]$$

$$= p . N . (p+q)^{N-1}$$

$$\Rightarrow \langle n_1 \rangle = pN (p+q)^{n-1}$$

If $p+q=1$, ~~therefore~~ e.g. unbiased walk, then

$$\langle n_1 \rangle = pN$$

Similarly,

$$\langle n_2 \rangle = qN$$

$${}^{N}C_{n_1} \sum_{n_1=0}^{N} {}^{N}C_{n_1} p^{n_1} q^{N-n_1} \cdot n_1$$

LECTURE - IV

$\Delta n_1 \equiv n_1 - \langle n_1 \rangle$ (defined as)

we need to find

$\langle \Delta n_1 \rangle$, $\langle \Delta n_2 \rangle$, $\langle \Delta m \rangle$ & $\langle m \rangle$

$\langle (\Delta n_1)^2 \rangle$, $\langle (\Delta n_2)^2 \rangle$, $\langle (\Delta m)^2 \rangle$

this quantity can be measured experimentally for any solute in a solvent.

$$W_N(n_1) = \frac{N!}{(n_1!)(n_2!)} \cdot p^{n_1} \cdot q^{n_2} = \frac{N!}{n_1! \cdot n_2!} \cdot p^{n_1} q^{N-n_1}$$

$$\langle n_1 \rangle = pN, \quad \langle n_2 \rangle = qN$$

$$\left(= \sum_{n_1=0}^{N} n_1 W_N(n_1) \right)$$

$$\langle m \rangle = \langle n_1 - n_2 \rangle = \langle n_1 \rangle - \langle n_2 \rangle = pN - qN$$

$$\Rightarrow \langle m \rangle = (p-q)N$$

e.g. for unbiased random walk, $\langle m \rangle = 0$

Now,

$$\langle (\Delta n)^2 \rangle = \langle (n_1 - \langle n_1 \rangle)^2 \rangle$$

$$\langle (\Delta n)^2 \rangle = \langle n_1^2 \rangle - \langle n_1 \rangle^2$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^{N} n_1^2 \cdot W_N(n_1) = \sum_{n_1=0}^{N} {}^{N}C_{n_1} \cdot p^{n_1} q^{N-n_1} n_1^2$$

$$\frac{\partial^2}{\partial p^2} p^{n_1} = n_1(n_1-1)p^{n_1-2} \quad \Big| \quad n_1 p^{n_1} =$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^{N} n_1^2 \cdot {}^N C_{n_1} p^{n_1} q^{n_2}$$

$$n_1 p \frac{\partial}{\partial p} p^{n_1} = n_1^2 p_1^{n_1} \quad \cancel{= p^2 \frac{\partial^2}{\partial p^2} p^{n_1}}$$

$$\cancel{p \frac{\partial}{\partial p}\left(p \frac{\partial}{\partial p} p^{n_1}\right) = n_1^2 p_1^{n_1-}}$$

$$\cancel{= \sum_{n_1=0}^{N} {}^N C_{n_1} \cdot n_1 \cdot p \frac{\partial}{\partial p} p^{n_1} \cdot p^{n_1} q^{n_2}}$$

$$\cancel{= p \frac{\partial}{\partial p}\left[\sum_{n_1=0}^{N} {}^N C_{n_1} \cdot p^{n_1} q^{N-n_1} \cdot n_1\right]}$$

$$\cancel{= p \frac{\partial}{\partial p} \langle n_1 \rangle} \qquad n_1 p \frac{\partial}{\partial p} p^{n_1} = n_1^2 p_1^{n_1}$$

$$\cancel{\langle n_1^2 \rangle = \sum_{n_1=0}^{N} n_1^2 \cdot {}^N C_{n_1} \cdot p^{n_1} q^{N-n_1}}$$

$$\cancel{n_1^2 p^{n_1} = n_1}$$

$$n_1 p^{n_1} = p \frac{\partial}{\partial p} p^{n_1}$$

$$n_1^2 p^{n_1} = p \frac{\partial}{\partial p}\left(p \frac{\partial}{\partial p} p^{n_1}\right) = p\left[p \frac{\partial^2}{\partial p^2} p^{n_1} + \frac{\partial}{\partial p} p^{n_1}\right]$$

$$\cancel{= p \frac{\partial}{\partial p} p^{n_1} + p \frac{\partial}{\partial p} p^{n_1}}$$

$$= p^2 \frac{\partial^2}{\partial p^2} p^{n_1} + p \frac{\partial}{\partial p} p^{n_1}$$

$$p^2 \frac{\partial}{\partial p} p^{n_1} \qquad p^{n_1} \qquad n_1(n_1-1) \quad \frac{\partial^2}{\partial p^2}$$

$$\langle n_1^2 \rangle = \sum_{n_1=0}^{N} {}^N C_{n_1} \, q^{N-n_1} \left(p^2 \frac{\partial^2}{\partial p^2} p^{n_1} + p \frac{\partial}{\partial p} p^{n_1} \right)$$

$$= p^2 \frac{\partial^2}{\partial p^2} \left[\sum_{n_1=0}^{N} {}^N C_{n_1} q^{N-n_1} \cdot p^{n_1} \right] + p \frac{\partial}{\partial p} \left[\sum_{n_1=0}^{N} {}^N C_{n_1} \cdot p^{n_1} q^{N-n_1} \right]$$

$$= p^2 \cdot \frac{\partial^2}{\partial p^2} \left[(p+q)^N \right] + p \frac{\partial}{\partial p} \left[(p+q)^N \right]$$

$$= p^2 \left[N(N-1)(p+q)^{N-2} \right] + pN(p+q)^{N-1}$$

$$\langle n_1^2 \rangle = p^2 \left[N^2 - N \right] + pN$$

$$= p^2 N^2 - Np^2 + pN$$

$$= p^2 N^2 + pN(1-p)$$

$$\langle n_1^2 \rangle = (pN)^2 + pqN$$

$$\therefore \langle (\Delta n_1)^2 \rangle = \langle n_1^2 \rangle - \left(\langle n_1 \rangle \right)^2$$

$$= (pN)^2 + pqN - (pN)^2$$

$$\boxed{\langle (\Delta n_1)^2 \rangle = pqN}$$

Root mean square deviation of $n_1 = \sqrt{\langle (\Delta n_1^2) \rangle} = \Delta^* n_1$

$$\Rightarrow \Delta^* n_1 = \sqrt{\langle (\Delta n_1)^2 \rangle}$$

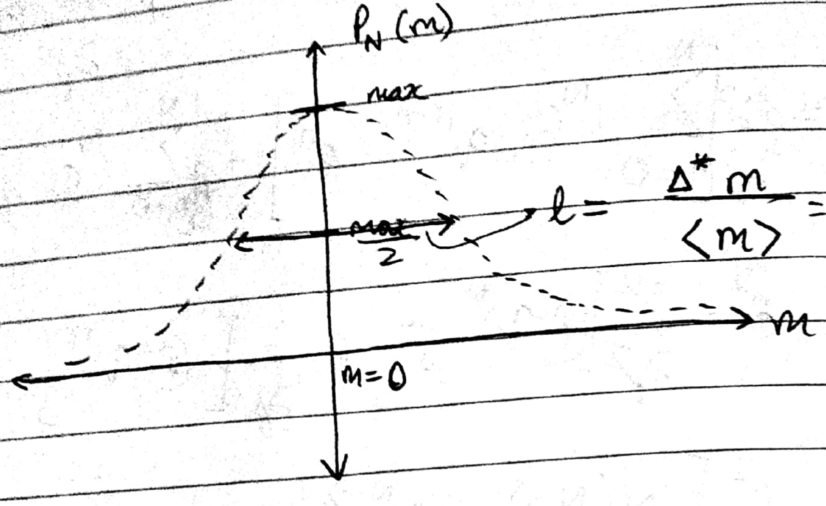
$$= \sqrt{Npq}$$

Similarly,

$$\langle (\Delta n_2)^2 \rangle = pqN$$

$$\therefore \Delta^* n_2 = \sqrt{pqN}$$

The relative width of the distribution of $n_1 \equiv \frac{\Delta^* n_1}{\langle n_1 \rangle}$



For n_1, relative width of distribution $= \frac{\sqrt{pqN}}{pN}$

$= \sqrt{\frac{q}{pN}}$

$\therefore$ For unbiased case,

~~relative~~ width $= \frac{1}{\sqrt{N}}$

Width measures the spread of data and is, in some sense, the error in measurement.

So here, error decreases with number of measurement.

$\langle (\Delta m)^2 \rangle = \langle m_1^2 \rangle - \left(\langle m_1 \rangle\right)^2 = 4 \langle (\Delta n_1)^2 \rangle$

as

$m = n_1 - n_2 = 2n_1 - N$

$\Delta m = m - \langle m \rangle$

$= 2n_1 - \cancel{N} - \langle 2n_1 \rangle + \cancel{N}$

$= 2[n_1 - \langle n_1 \rangle] = 2\Delta n$

$\Rightarrow (\Delta m)^2 = 4(\Delta n)^2$

$\therefore$ $$\boxed{\langle(\Delta m)^2\rangle = 4\,\langle(\Delta n)^2\rangle}$$

$$\langle(\Delta m)^2\rangle = 4pqN$$

$$\therefore \quad \Delta^* m = 2\sqrt{pqN}$$

e.g. for unbiased case,

$$\Delta^* m = \sqrt{N}$$

Also, in general,

$$\langle(\Delta m)^2\rangle \propto N$$

$$\cancel{\langle(\Delta m)^2\rangle = \langle m^2 + \langle m\rangle^2 - 2m\langle m\rangle\rangle = \langle m^2\rangle + \langle m\rangle^2 - 2\langle m\rangle\langle m\rangle}$$

Since $\Delta m = 0$ for unbiased random walker,

$$\underbrace{\langle m^2\rangle}_{\text{mean square displacement}} \propto N$$

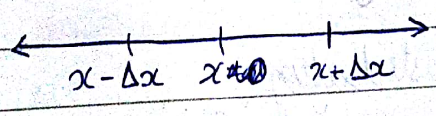
$\therefore$ Mean square displacement of random walker increases linearly with time.

LECTURE-V

For random ~~distribution~~ diffusion,

$$\underbrace{\langle x^2\rangle}_{\text{random diffusion}} \propto \text{time}$$

→ Derivation of the Diffusion Equation from the random walk model (one dimensional)



$\Delta x \rightarrow$ step length of random walker

$$\frac{d^2}{dt^2}f(t) = \lim_{h_2\to 0}\lim_{h_1\to 0} \frac{\frac{f(x_0+h_1+h_2)-f(x_0+h_2)}{h_1} - \frac{f(x+h)-f(x)}{h}}{h}$$

$$= \lim_{h\to 0} \frac{f(x+2h)-2f(x+h)+f(x)}{h}$$

$P(x,t)$ → probability that random walker is at x at time t.

We try to find $P(x, t+\Delta t)$

$P(x, t+\Delta t) = ?$

Δt – the timestep

In fact

$$P(x, t+\Delta t) = P(x+\Delta x, t)\,\Pi(x+\Delta x \to x)$$
$$+ P(x-\Delta x, t)\,\Pi(x-\Delta x \to x)$$
$$- P(x,t)\,\Pi(x \to x+\Delta x)$$
$$- P(x,t)\,\Pi(x \to x-\Delta x)$$

↳ transitional probability i.e. probability to move from $x+\Delta x \to x$

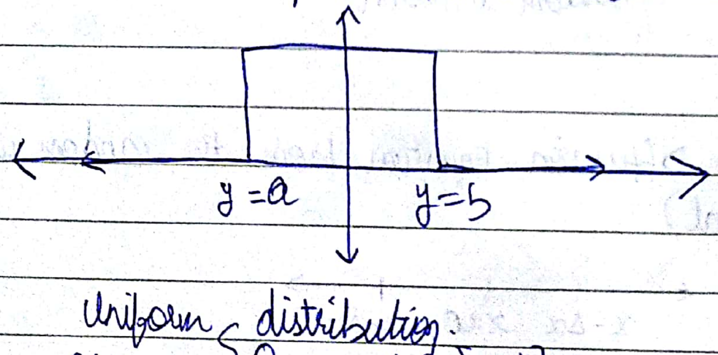
For an unbiased random walker,

$$\Pi(x \to x+\Delta x) = \Pi(x \to x-\Delta x) = \frac{1}{2}$$

i.e. all transitional probabilities is equal to 0.5

$$\therefore P(x, t+\Delta t) - P(x,t) = \frac{1}{2}\left[P(x+\Delta x, t) - 2P(x,t) + P(x-\Delta x, t)\right]$$

Computational Exercise

① 

Uniform distribution:

$$P(y) = \begin{cases} 0, & y \notin [a,b] \\ \frac{1}{b-a}, & y \in [a,b] \end{cases}$$

$$\frac{dx}{dt} = \lim_{h \to 0} \frac{f(x+h) - f(x)}{h}$$

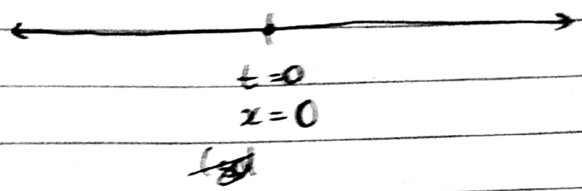
Range: $y \in [0,1]$ i.e. $a = 0, b = 1$

If $y < \frac{1}{2}$, x moves left else it moves right

LECTURE - VI
23 August 2018

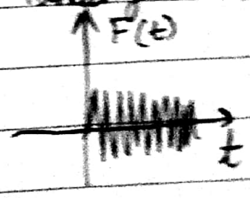
Langevin Dynamics
Mathematical model for diffusion of solute in a solvent

One dimensional case -



Solute at $x = 0$, at $t = 0$, in a solvent
Two forces - viscous force, which resists motion of particle, and a random force, which acts on the particle randomly
$m \to$ mass of particle
$x(t) \to$ position of particle at time t
Equation of motion -

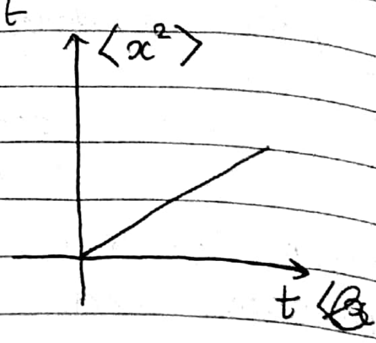
$$m\frac{d\dot{x}}{dt} = \underbrace{-\alpha \dot{x}}_{\substack{\text{damping force} \\ (\alpha > 0 \text{ is friction coefficient})}} + \underbrace{F(t)}_{\substack{\text{random force} \\ (\text{fluctuates randomly with } t)}} \quad \text{— (1)}$$



$\langle F \rangle = 0$

What is $\langle x^2 \rangle$ of the solute?

For a random walk, $\langle x^2 \rangle \propto t$



$$m\frac{d\dot{x}}{dt} = -\alpha\dot{x} + F(t)$$

Multiplying with x on both side,

$$mx\frac{d\dot{x}}{dt} = -\alpha x\dot{x} + xF(t)$$

$$\Rightarrow m\left[\frac{d}{dt}(x\dot{x}) - (\dot{x})^2\right] = -\alpha x\dot{x} + xF(t)$$

Taking average on both sides,

$$m\left[\left\langle \frac{d}{dt}(x\dot{x})\right\rangle - \left\langle (\dot{x})^2 \right\rangle\right] = -\alpha\langle x\dot{x}\rangle + \langle xF(t)\rangle$$

$$= -\alpha\langle x\dot{x}\rangle + \langle x\rangle\langle F(t)\rangle$$

as x, $F(t)$ are uncorrelated i.e independence.

∴ Since $\langle F(t)\rangle =$

$$m\left[\left\langle \frac{d}{dt}(x\dot{x})\right\rangle - \left\langle \dot{x}^2\right\rangle\right] = -\alpha\langle x\dot{x}\rangle \quad -(2)$$

We know that mean K.E ⟨K⟩ is

$$\langle K\rangle = \frac{1}{2}k_BT = \frac{1}{2}m\langle\dot{x}^2\rangle$$

k_B - Boltzmann Constant
T - temparature

From (2),

$$m\left[\left\langle\frac{d}{dt}(x\dot{x})\right\rangle - \frac{k_BT}{m}\right] = -\alpha\langle x\dot{x}\rangle$$

$$\Rightarrow m\left\langle\frac{d}{dt}(x\dot{x})\right\rangle = k_BT - \alpha\langle x\dot{x}\rangle$$

Also, $\left\langle\frac{du}{dt}\right\rangle = \frac{d}{dt}\langle u\rangle$

$$\therefore \quad m\frac{d}{dt}\langle x\dot{x}\rangle = k_BT - \alpha\langle x\dot{x}\rangle \quad -(3)$$

This is a 1st order linear Differential equation in $\langle x\dot{x}\rangle$.

∴ Solution is

$$\langle x\dot{x}\rangle = \frac{k_BT}{\alpha} + ce^{-\gamma t} \quad -(4)$$

Here, c is the constant of integration.

$$\gamma = \frac{\alpha}{m}$$

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~~Note at t=0~~

Note that,

$$\langle x\dot{x}\rangle = \frac{1}{2}\frac{d}{dt}\langle x^2\rangle$$

Equation 4 implies

$$\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = ce^{-\gamma t} + \frac{k_B T}{\alpha}$$

According to initial condition at $t=0$, $x=0$

$$\therefore \quad c = -\frac{k_B T}{\alpha} \quad (\text{at } t=0,\ \langle x^2\rangle = 0)$$

$\therefore$ 4 becomes

$$\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = \frac{k_B T}{\alpha}\left(1 - e^{-\gamma t}\right) \quad (5)$$

Integrating from $t=0$ to $t=t$,

$$\langle x^2\rangle = \frac{2k_B T}{\alpha}\left[t - \left(-\frac{e^{-\gamma t}}{\gamma} + \frac{1}{\gamma}\right)\right]$$

$$\Rightarrow \boxed{\langle x^2\rangle = \frac{2k_B T}{\alpha}\left[t - \left(\frac{1-e^{-\gamma t}}{\gamma}\right)\right]} \quad (6)$$

$$+ \frac{e^{-\gamma t}}{\gamma}\Big|_0^t \qquad \frac{d}{dt}\langle x^2 \rangle = \left\langle \frac{d}{dt}(x^2) \right\rangle$$

Limiting cases :-

1) When $t << \frac{1}{\gamma} \Rightarrow 0 < \gamma t << 1$ (short time diffusion)

$$\cancel{\therefore \gamma t \approx 0, \; e^{-\gamma t}}$$

$$\cancel{\therefore \langle x^2 \rangle = \frac{2k_BT}{\alpha}[t] = 0}$$

$$\because e^{-\gamma t} = 1 - \gamma t + \underbrace{\frac{\gamma^2 t^2}{2} + \dots}$$

neglecting higher powers as $\gamma t << 1$,

$$e^{-\gamma t} = 1 - \gamma t + \frac{1}{2}\gamma^2 t^2$$

$$\cancel{\langle x^2 \rangle = \frac{2k_BT}{\alpha}\left(t - \frac{\gamma t}{\gamma}\right) = 0}$$

$$\therefore \langle x^2 \rangle = \frac{2k_BT}{\alpha}\left[t - \frac{1}{\gamma}\left(1 - \left(1 - \gamma t + \frac{1}{2}\gamma^2 t^2\right)\right)\right]$$

$$= \frac{2k_BT}{\alpha}\left[t - \frac{1}{\gamma}\left(\gamma t - \frac{1}{2}\gamma^2 t^2\right)\right]$$

$$\langle x^2 \rangle = \frac{\cancel{2}k_BT}{\alpha}\gamma t^2 = \left(\frac{k_BT}{m}\right)t^2$$

This is similar to a free particle with no force as

$$\frac{d\dot{x}}{dt} = 0 \Rightarrow x \propto t \Rightarrow x^2 \propto t^2 \Rightarrow \langle x^2 \rangle \propto t^2$$

∴ Solute behaves like a free particle for a short ~~particle~~ period of time

$$\sum_{n_1=0}^{\infty} W_N^2(n_1) = \sum_{n_1=0}^{\infty}\left[\frac{(N!)}{(n_1)!(N-n_1)!}\left(\frac{1}{2}\right)^N\right]^2$$

2.) Long time limit i.e

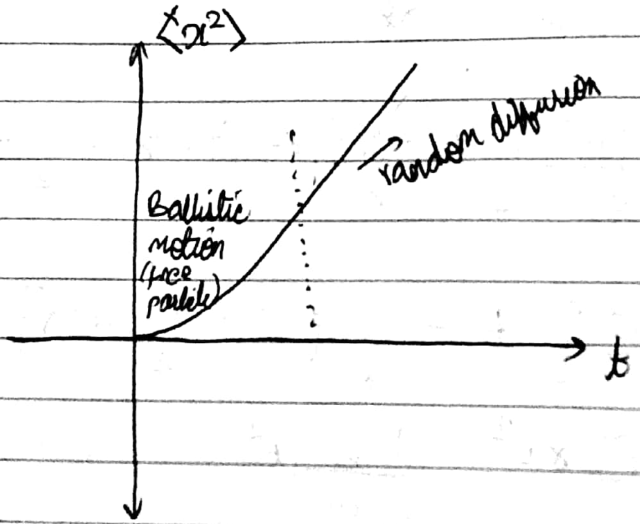
$$t >> \frac{1}{\gamma} \Rightarrow \gamma t >> 1$$

$$\therefore e^{-\gamma t} \approx 0$$

$$\therefore \langle x^2 \rangle = \frac{2k_BT}{\alpha}\left(t - \frac{(1-\cancel{e^{-\gamma t}})}{\gamma}\right)$$

$$= \frac{2k_BT}{\alpha}\left(t - \frac{1}{\gamma}\right)$$

∴ After a very long time it tends to linear time dependence ie it tends to a random walk.

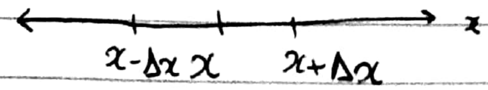


Class Assignment - I :-

Two drunks start out at the origin, each having equal probabilities of making a step to the left or right along the x-axis. Find the probability that they meet again after N steps. It is to be understood that the men take their steps simultaneously.

LECTURE – VII

Derivation of the ~~differential~~ diffusion equation from random walk Model (one-dimensional case) –



$\Delta x \rightarrow$ step length in a given time step Δt

It is an unbiased random walker.

Transition Probabilities –

$$\Pi(x+\Delta x \rightarrow x) = 1/2$$

$$\Pi(x-\Delta x \rightarrow x) = 1/2$$

$$\Pi(x \rightarrow x+\Delta x) = 1/2$$

$$\Pi(x \rightarrow x-\Delta x) = 1/2$$

$\mathbb{P}(x,t) \Rightarrow$ probability of finding the random walker at x at time t.

The change in probability can be written as

$$\mathbb{P}(x, t+\Delta t) - \mathbb{P}(x,t)$$

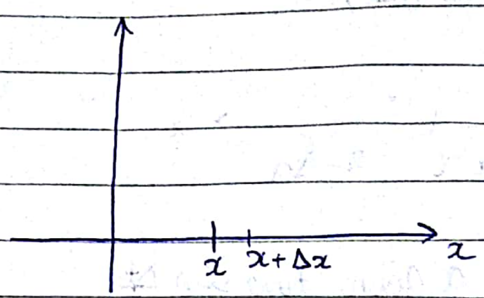
$$= -\Pi(x \rightarrow x+\Delta x)\, \mathbb{P}(x,t) - \Pi(x \rightarrow x-\Delta x)\, \mathbb{P}(x,t) + \Pi(x+\Delta x \rightarrow x)\, \mathbb{P}(x+\Delta x, t) + \Pi(x-\Delta x \rightarrow x)\, \mathbb{P}(x-\Delta x, t)$$

(or

$$\mathbb{P}(x, t+\Delta t) = \mathbb{P}(x+\Delta x, t)\, \Pi(x+\Delta x \rightarrow x) + \mathbb{P}(x-\Delta x, t)\, \Pi(x-\Delta x \rightarrow x)$$
)

$$P(x, t+\Delta t) - P(x,t) = \frac{1}{2}\left[P(x+\Delta x, t) - 2P(x,t) + P(x-\Delta x, \ldots\right] \quad (1)$$

Taylor's Series expansion:-



We know $f(x)$, $f'(x)$, $f''(x)$, $f^{n}(x)$ at x

i.e we know

$$f(x), \left.\frac{df(x)}{dx}\right|_x, \left.\frac{d^2f}{dx^2}\right|_x, \ldots \left.\frac{d^n f(x)}{dx^n}\right|_x$$

Then, for sufficiently small Δx,

~~f(x)(x+Δx)~~

$$f(x+\Delta x) = \frac{1}{0!}f(x) + \frac{1}{1!}\left.\frac{df}{dx}\right|_x \Delta x + \frac{1}{2!}\left.\frac{d^2f}{dx^2}\right|_x (\Delta x)^2 + \ldots + \frac{1}{n!}\left.\frac{d^nf}{dx^n}\right|_x (\Delta x)^n + \ldots\ldots$$

$$\therefore P(x+\Delta x, t) = P(x,t) + \frac{\partial P(x,t)}{\partial x} \cdot \Delta x + \frac{1}{2!}\frac{\partial^2 P(x,t)}{\partial x^2}(\Delta x)^2 + \ldots\ldots$$

similarly,

$$P(x-\Delta x, t) = P(x,t) - \frac{\partial P(x,t)}{\partial x}\Delta x + \frac{1}{2!}\frac{\partial^2 P(x,t)}{\partial x^2}(\Delta x)^2 - \ldots\ldots$$

W

For sufficiently small Δx, we ignore $(\Delta x)^n$ for $n > 2$.

$\therefore$ For $\Delta x \to 0$,

$$P(x+\Delta x, t) + P(x-\Delta x, t) = 2P(x,t) + \frac{\partial^2 P(x,t)}{\partial x^2}(\Delta x)^2$$

$$\Rightarrow \underbrace{P(x+\Delta x, t) - 2P(x,t) + P(x-\Delta x, t)}_{②} = \left[\frac{\partial^2}{\partial x^2} P(x,t)\right](\Delta x)^2$$

Putting in ①,

$$\therefore P(x, t+\Delta t) - P(x,t) = \frac{1}{2}\left[\frac{\partial^2}{\partial x^2} P(x,t)\right](\Delta x)^2$$

Note :-

② can also be derived in the following way

$$g(x) = \frac{d}{dx} f(x) = \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

$$h(x) = \frac{d}{dx} g(x) = \frac{d^2 f(x)}{dx^2} = \lim_{\Delta x \to 0} \frac{g(x+\Delta x) - g(x)}{\Delta x}$$

$$= \lim_{\Delta x \to 0} \cancel{\lim_{\Delta x \to 0}} \frac{f(x+2\Delta x) - 2f(x+\Delta x) + f(x)}{(\Delta x)^2}$$

$$= \lim_{\Delta x \to 0} \frac{f(x+\Delta x) - 2f(x) + f(x-\Delta x)}{(\Delta x)^2}$$

$\therefore$ For small Δx,

$$f(x+\Delta x) - 2f(x) + f(x-\Delta x) = (\Delta x)^2 \cdot \frac{d^2 f(x)}{dx^2}$$

$$\beta C e^{\alpha x + \beta t} = D\alpha^2 e^{\alpha x + \beta t}$$

$$\beta C = \alpha^2 D$$

$\therefore$ For $\Delta x \to 0$

$$P(x, t+\Delta t) - P(x,t) = \frac{1}{2}\left(\frac{\partial^2 P(x,t)}{\partial x^2}\right)(\Delta x)^2$$

$$\Rightarrow \frac{P(x, t+\Delta t) - P(x,t)}{\Delta t} = \frac{1}{2}\left(\frac{\partial^2 P(x,t)}{\partial x^2}\right)\cdot\frac{(\Delta x)^2}{\Delta t}$$

Now, for $\Delta t \to 0$,

$$\underbrace{\frac{\partial P(x,t)}{\partial t}}_{\text{time derivative}} = \frac{1}{2}\frac{(\Delta x)^2}{\Delta t}\cdot\underbrace{\frac{\partial^2 P(x,t)}{\partial x^2}}_{\text{spacial derivative}}$$

Let $D = \dfrac{(\Delta x)^2}{2\Delta t}$

D is called the diffusion constant or diffusion coefficient

$$\therefore \boxed{\frac{\partial P(x,t)}{\partial t} = D\cdot\frac{\partial^2 P(x,t)}{\partial x^2}}$$

Diffusion equation

In general, if we solve the diffusion equation, we can determine $P(x,t)$ (given the initial conditions).

For 3-D, the diffusion equation is, given that $\vec{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$

$P(\vec{r}, t)$

$$\frac{\partial^2}{\partial x^2} f(x,y) = 0$$

$$\Rightarrow \frac{\partial}{\partial x} f(x,y) = g(y) \Rightarrow f(x,y) = x\, g(y)$$

$$\frac{\partial}{\partial x} f(x,y) = 0 \Rightarrow f(x,y) = g(y)$$

$$\frac{\partial}{\partial x} f(x,y) = \frac{\partial}{\partial y} f(x,y)$$

$$\boxed{\frac{\partial P(\vec{r},t)}{\partial t} = D_x \frac{\partial^2 P(\vec{r},t)}{\partial x^2} + D_y \frac{\partial^2}{\partial y^2} P(\vec{r},t) + D_z \frac{\partial^2}{\partial z^2} P(\vec{r},t)}$$

D_x, D_y, D_z – diffusion coefficient along the 3 axes

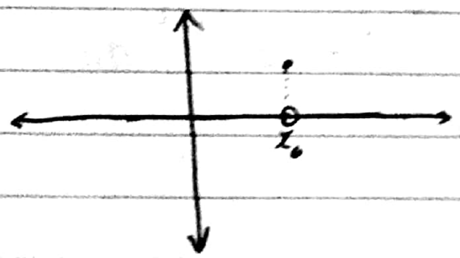
For a homogenous medium

$$D_x = D_y = D_z = D$$

→ Solving the diffusion equation (1-D)

Initial condition :- $P(x, t=0) = \delta(x - x_0)$, where

$\delta(x)$ is a function 0 everywhere but $x_0 = 0$



For our case, take $x_0 = 0$

$$\therefore P(x,0) = \delta(x)$$

LECTURE VIII

Diffusion equation :-

$$\frac{\partial P(x,t)}{\partial t} = D \frac{\partial^2 P(x,t)}{\partial x^2}$$

Initial condition :-

$$P(x,0) = \delta(x)$$

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$$\int uv\,dx = u\int v\,dx - \int \frac{du}{dx}\left(\int v\,dx\right)dx$$

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty} P(x,t)\,dx\right)dk \quad e^{ikx}$$

We use Fourier Transformation technique to solve the problem.

Fourier Transformation :-

$$\tilde{P}(k,t) \overset{\text{defined as}}{\triangleq} \int_{-\infty}^{\infty} P(x,t)\, \underbrace{e^{ikx}}_{\text{kernel}}\, dx$$

k:- ~~Re~~ element in inverse space of x-space
e.g. we can move from time domain t to angular frequency ($\frac{2\pi}{t}$) space.

Here we move from ~~Re~~ real-space to inverse space.

Laplace Transform:- Similar to Fourier transform, but we use e^{-kx}

Inverse Fourier Transform:-

$$P(x,t) \triangleq \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{P}(k,t)\, e^{-ikx}\, dk$$

Now,

We calculate the Fourier transform of $\frac{\partial P(x,t)}{\partial t}$ and $\frac{\partial^2 P}{\partial x^2}$

①

$$\widetilde{\frac{\partial P(k,t)}{\partial t}} = \int_{-\infty}^{\infty} \frac{\partial P(x,t)}{\partial t}\, e^{ikx}\, dx$$

$$= \frac{\partial}{\partial t}\int_{-\infty}^{\infty} P(x,t)\, e^{ikx}\, dx$$

$$\widetilde{\frac{\partial P(k,t)}{\partial t}} = \frac{\partial}{\partial t}\tilde{P}(k,t) \quad -①$$

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$\int uv\,dx = u\int v\,dx - \int\left(\int v\,dx\right)dx$ $\quad \frac{1}{2\pi}\int_{-\infty}^{\infty}\left(\int_{-\infty}^{\infty} P(x,t)\, e^{ikx}\,dx\right)e^{-ikx}\,dk$

$$\widetilde{\frac{\partial}{\partial x} P(k,t)} = \int_{-\infty}^{\infty} \frac{\partial}{\partial x} P(x,t)\, e^{ikx}\,dx$$

By using integration by parts,

$$= \left[e^{ikx} \cdot P(x,t)\right]_{-\infty}^{\infty} - ik\int_{-\infty}^{\infty} P(x,t)\cdot e^{ikx}\,dx$$

For $x \to \pm\infty$, and finite t, $P(x,t) \to 0$, $\frac{\partial P(x,t)}{\partial x} \to 0$

$$\therefore \widetilde{\frac{\partial P(k,t)}{\partial x}} = -ik \cdot \tilde{P}(k,t) \quad -①$$

Now, $$\widetilde{\frac{\partial^2 P(k,t)}{\partial x^2}} = \int_{-\infty}^{\infty} \frac{\partial^2}{\partial x^2} P(x,t) e^{ikx}\,dx$$

$$= \left[e^{ikx} \cdot \frac{\partial P(x,t)}{\partial x}\right]_{-\infty}^{\infty} - ik\int_{-\infty}^{\infty} \frac{\partial P(x,t)}{\partial x} e^{ikx}\,dx$$

As $\frac{\partial}{\partial x} P(x,t) \to 0$ as $x \to \pm\infty$,

$$\widetilde{\frac{\partial^2 P(x,t)}{\partial x^2}} = -ik\, \widetilde{\frac{\partial P(x,t)}{\partial x}} = -ik\left(-ik\,\tilde{P}(k,t)\right)$$
(from ①)

$$\Rightarrow \widetilde{\frac{\partial^2 P(k,t)}{\partial x^2}} = -k^2\, \tilde{P}(k,t)$$

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∴ In ~~the~~ ~~phase space~~ k-space, diffusion equation becomes

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2}$$

Taking Fourier transform on both sides, and simplifying

$$\frac{\partial}{\partial t}\left(\tilde{P}(k,t)\right) = D.(-k^2\tilde{P}(k,t))$$

$$\frac{\partial \tilde{P}(k,t)}{\partial t} = -Dk^2\tilde{P}(k,t)$$

First order D.E,

Solving this, we get

$$\tilde{P}(k,t) = C\cdot e^{-Dk^2 t}$$

From initial condition

$$\cancel{P(x,0) = \delta(x) = \begin{cases} 1 & x=0 \\ 0 & \text{elsewhere} \end{cases}}$$

$$P(x=0, t=0) = 1$$

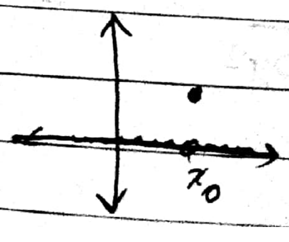
$$P(x,0) = \underbrace{\delta(x)}_{\text{Dirac Delta function}}$$

Dirac Delta function ~~at x=0~~

$$\therefore \tilde{P}(k,0) = \int_{-\infty}^{\infty} \delta(x).e^{ikx}\,dx = C$$

$$\Rightarrow C = \int_{-\infty}^{\infty} \delta(x-x_0).e^{ikx}\,dx, \quad x_0 = 0$$

$\delta(x-x_0)$

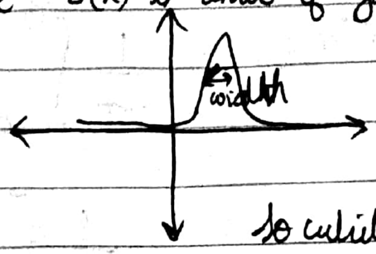


$$\frac{\partial}{\partial t} f(k,t) = -Dk^2 f(k,t)$$

$\therefore C = e^{ikx_0}$ (this is because $\delta(x)$ is limit of Gaussian as width $\to 0$

since $x_0 = 0$,

$C = 1$



so while integrating we integrate Gaussian and then take the limit.)

$$\therefore \tilde{P}(k,t) = e^{-Dk^2 t}$$

Now, we apply the inverse Fourier transform.

$$\therefore P(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{P}(k,t) \cdot e^{-ikx}\, dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dk^2 t} \cdot e^{-ikx}\, dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-(Dk^2 t + ikx)}\, dk$$

Let $a^2 = Dk^2 t$, $2ab = ikx$

$$\Rightarrow b = \frac{ix}{2\sqrt{Dt}}$$

Adding and subtracting b^2 in exponent,

$$P(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-\left[Dk^2t + ikx + \left(\frac{ix}{2\sqrt{Dt}}\right)^2\right] + \left(\frac{ix}{2\sqrt{Dt}}\right)^2} dk$$

$$= \frac{1}{2\pi} e^{\left(\frac{ix}{2\sqrt{Dt}}\right)^2} \cdot \int_{-\infty}^{\infty} e^{-(a+b)^2} dk$$

$$\Rightarrow P(x,t) = \frac{1}{2\pi} e^{-x^2/4Dt} \cdot \int_{-\infty}^{\infty} e^{-(a+b)^2} dk$$

$$\cancel{= \frac{1}{2\pi} e^{-\frac{x^2}{4Dt}} \int_{-\infty}^{\infty} e^{-\left(k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}\right)^2} dk}$$

Let $y = a+b = k\sqrt{Dt} + \frac{ix}{2\sqrt{Dt}}$

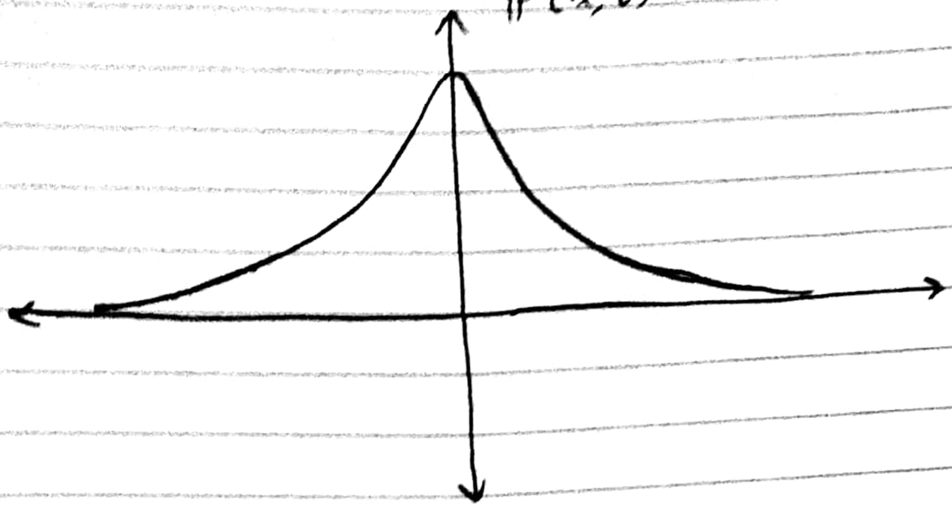
$$\Rightarrow dy = \sqrt{Dt} \cdot dk$$

$$\therefore P(x,t) = \frac{1}{2\pi} e^{-\frac{x^2}{4Dt}} \cdot \int_{-\infty}^{\infty} \frac{e^{-y^2}}{\sqrt{Dt}} dy$$

$$= \frac{1}{2\pi\sqrt{Dt}} \cdot e^{-\frac{x^2}{4Dt}} \underbrace{\int_{-\infty}^{\infty} e^{-y^2} dy}_{\text{Gaussian}}$$

$$\int_{-\infty}^{\infty} y e^{-y^2} dy = \sqrt{\pi}$$

$$\therefore \boxed{P(x,t) = \frac{1}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}}$$



For the 3-D case, solving equation yields

$$P(\vec{r},t) = \frac{1}{(4\pi Dt)^{3/2}} \, e^{-\frac{(x^2+y^2+z^2)}{4Dt}}$$

$$= \frac{1}{(4\pi Dt)^{3/2}} \cdot e^{-\frac{|\vec{r}|^2}{4Dt}}$$