Langevin Theory of the "Brownian Motion" :–

The continuous zig-zag motion colloidal particles in the medium is called "Brownian motion".

This is due to the unequal bombardments of of the moving molecules of medium on colloidal particles. As the particle moves in a particular direction, other molecules of the medium again collide with it and the particle changes its directions, This result in a random zig-zag movement of the colloidal particle.

Let us consider the simple case of a free Brownian particle, surrounded by a fluid environment. This is assumed to be free in the sense that it is not acted upon by any other force except the force due to molecular bombardment. Thus the eq^n of motion of the particle will be

$$M\frac{dv}{dt} = F(t) \qquad \text{—— (1)}$$

where, M is the mass of the particle.
v(t) is the velocity of the particle at time t
F(t) is the force acting upon the particle by virtue of the impacts from fluid molecules.

Langevin suggested that the force F(t) can be written as a some of two parts:–

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i) An averaged out part which represents the viscous $-v/B$, experienced by the particle. In this, B is the mobility of the system. i.e., the drift velocity velocity acquired by the particle by virtue of a unit external force.

ii) A rapidly fluctuating part F(t) which overlong intervals of time averages out to zero. Thus we can write,

$$M\frac{dv}{dt} = \frac{-v}{B} + F(t) \; ; \; \overline{F(t)} = 0 \quad \text{——— (2)}$$

Taking the ensemble average of eq^n (2), we obtain,

$$M\frac{dv}{dt} = \frac{-1}{B}(v) \quad \text{——— (3)}$$

when,

$$\langle v(t)\rangle = v(0)\exp\left(\frac{-t}{\tau}\right) \quad \text{——— (4)}$$

where $\tau = MB$

Thus, the mean drift velocity of the particles decays of a rate determined by the relaxation time τ to the ultimate value zero.

Now, From the eqⁿ (2), we have,

$$\frac{dv}{dt} = \frac{-v}{MB} + \frac{F(t)}{M}$$

$$\Rightarrow \frac{dv}{dt} = -\frac{v}{\tau} + A(t), \quad \overline{A(t)} = 0 \quad \text{———} \quad (5)$$

Eqⁿ (5) is called an eqⁿ for the instantanous acceleration.

We construct the scalar product of eqⁿ (5) with the instantaneous position r of the particle and take the ensemble average of the product.

Considering the facts that:

i) $r \cdot v = r \cdot v = \frac{1}{2}\left(\frac{dr^2}{dt}\right)$

ii) $r \cdot \left(\frac{dv}{dt}\right) = \frac{1}{2}\left(\frac{d^2 r^2}{dt^2}\right) - v^2$, and

iii) $r \cdot A = 0$

Thus, we obtain,

$$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2\langle v^2\rangle \quad \text{———} \quad (6)$$

If the Brownian particle has already attained thermal equilibrium with the molecules of the fluid, then the quantity $\langle v^2 \rangle$ in this eqn. may be replaced by its equipartition value $3KT/M$.
The eqn is then readily integrated, as

$$\langle r^2 \rangle = \frac{6kT \cdot \tau^2}{M} \left\{ \frac{t}{\tau} - \left(1 - e^{-t/\tau}\right) \right\} \qquad \text{—— (7)}$$

where the constants of integration have been so chosen that at $t=0$ both $\langle r^2 \rangle$ and its first time derivative vanishes. Thus, for $t \ll \tau$,

$$\langle r^2 \rangle = \frac{3kT}{M} t^2 = \langle v^2 \rangle t^2 \qquad \text{—— (8)}$$

which is consistent with the reversible eqn of motion whereby, we have,

$$r = vt \qquad \text{—— (9)}$$

For $t \gg \tau$

$$\langle r^2 \rangle \simeq \frac{6kT\tau}{M} t = (6BkT)t \qquad \text{—— (10)}$$

which is same as the Einstein - Smoluchowski result.
Thus, we obtain a relationship between the coefficients of diffusion D and the mobility B, i.e.

$$D = BkT \quad \text{—— (11)}$$

This relation is called Einstein relation.

The Einstein relation (11) connects the coefficients of diffusion D with the mobility B of the system and tells us that the ultimate source of the viscosity of the medium as well as diffusion lies in the random, fluctuating forces arrising from the incessant motion of the fluid moleculer.

Let us consider a particle of charge "e" and mass "M" moving in a viscous fluid under the influence of an external electric field of intesity $\vec{E}$, then the motion of the particle will be determined by the eqn

$$M\frac{d}{dt}\langle v\rangle = -\frac{1}{B}\langle v\rangle + eE \quad \text{—— (12)}$$

The terminal drift velocity of the particle is given by the expression $(eB)E$, where eB is the mobility of the system and is denoted by ~~the system~~ μ.

Thus eqn (11) can be written as

$$D = \frac{kT}{e}\mu \quad \text{—— (13)}$$

This relation is called Nernst equation (eqⁿ 13).

From eqⁿ 5, i.e.,

$$\frac{dv}{dt} = \frac{-v}{\tau} + A(t) \; ; \quad \overline{A(t)} = 0$$

we have not felt any direct influence of the fluctuating term $A(t)$, that appears in the eqⁿ of motion 5 of Brownian particle. For this, let us evaluate the quantity $\langle v^2(t) \rangle$ which is assumed to have attained its limiting value $3KT/M$.

For this evaluation, we replace the variable t in eqⁿ 5 by u. Multiplying both sides of the eqⁿ by $\{\exp(u/\tau)$, rearranging and integrating over du between the limits $u=0$ and $u=t$, we obtain the solution,

$$v(t) = v(0)\, e^{-t/\tau} + e^{-t/\tau} \int_0^t e^{u/\tau} A(u)\, du \quad \text{——— (14)}$$

Thus, the drift velocity $v(t)$ of the particle is also fluctuating function of time, since

$\langle A(u) \rangle = 0$ for all u, the average drift velocity is given by first term alone

$$\langle v(t) \rangle = v(0)\, e^{-t/\tau} \quad \text{——— (15)}$$

which is same as eq^n (14).

For, the mean square velocity $\langle v^2(t)\rangle$, from eq^n (14), we get

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + 2e^{-2t/\tau}\left[v(0)\int_0^t e^{u/\tau}\langle A(u)\rangle du\right]$$

$$+ e^{-2t/\tau}\int_0^t\int_0^t e^{(u_1+u_2)/\tau}\langle A(u_1)A(u_2)\rangle du_1 du_2 \quad \text{--- (16)}$$

The second term on R.H.S. of this eq^n is identically zero, because $\langle A(u)\rangle$ vanishes for all u.
In third term, we have the quantity $\langle A(u_1); A(u_2)\rangle$ which is a measure of the statistical correlation between the value of fluctuating variable A at time u_1 and its value at time u_2. this is called "autoe correlation" function of variable A and is denoted by a symbol $K_A(u_1;u_2)$ or $K(u_1,u_2)$.

We now evaluate the double integral appearing in eq^n (16)

$$I = \int_0^t\int_0^t e^{(u_1+u_2)/\tau} K(u_2-u_1)\,du_1\,du_2 \quad \text{--- (17)}$$

changing over to the variables,

$$S = \frac{1}{2}(u_1+u_2) \quad \text{and} \quad s = (u_2-u_1) \quad \text{--- (18)}$$

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The integrand becomes $\exp \frac{2S}{\tau} K(s)$, the element (dU_1, dU_2) gets replaced by the corresponding element (dS, ds).

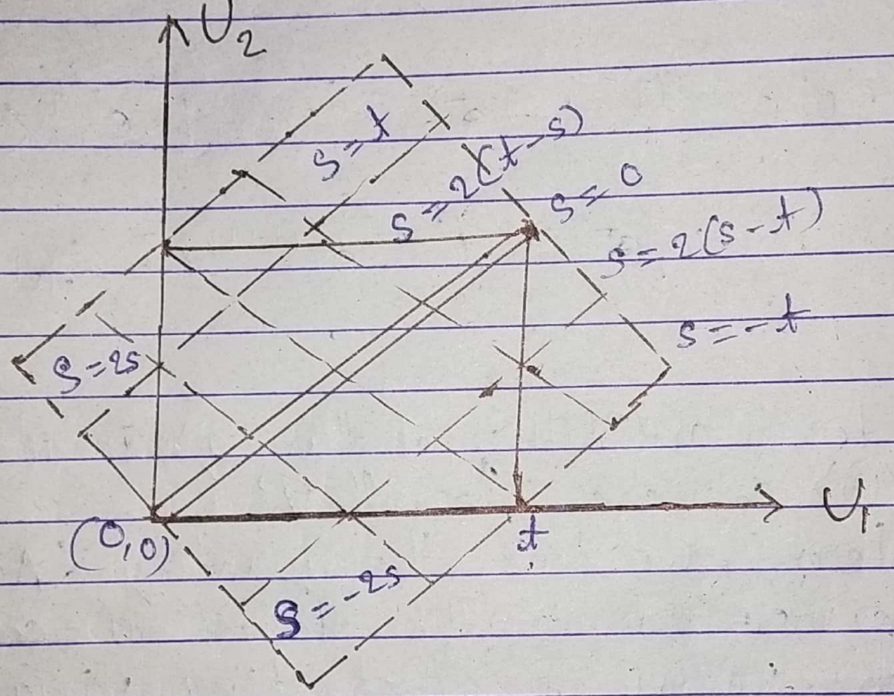

Fig (a)

From the following fig (a), we find that

for $0 \le S \le t/2$, s goes from $-2S$ to $+2S$, while for $t/2 \le S \le t$, s goes from $-2(t-S)$ to $+2(t-S)$

Accordingly,

$$I = \int_0^{t/2} e^{2S/\tau} \cdot dS \int_{-2S}^{2S} K(s)\,ds + \int_{t/2}^{t} e^{2S/\tau} \cdot dS \int_{-2(t-S)}^{2(t-S)} K(s) \cdot ds$$

If $t >> \tau^*$, the limits of integration for s may be replaced by $-\infty$ to $+\infty$, with the result

$$I \simeq c\int_0^t e^{2s/\tau}\,ds \doteq c\frac{\tau}{2}\left(e^{2t/\tau}-1\right) \quad \text{--- (20)}$$

where,

$$c = \int_{-\infty}^{\infty} K(s)\,ds \quad \text{--- (21)}$$

Substituting eqⁿ (20) into (16), we get

$$\langle v^2(t)\rangle = v^2(0)e^{-2t/\tau} + c\frac{\tau}{2}\left(1-e^{-2t/\tau}\right) \quad \text{--- (22)}$$

Now, as $t \to \infty$, $\langle v^2(t)\rangle$ must tend to equipartition value $3KT/M$, therefore

$$c = \frac{6KT}{M\tau}$$

Thus, $$\langle v^2(t)\rangle = v^2(0) + \left\{\frac{3KT}{M} - v^2(0)\right\}\left(1-e^{-2t/\tau}\right) \quad \text{--- (23)}$$

Substituting eqⁿ (23) in eqⁿ (6), we obtain a more representative description of the manner in which the quantity $\langle r^2\rangle$ varies with t, thus we have

$$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2v^2(0)\,e^{-2t/\tau} + \frac{6kT}{M}\left(1-e^{-2t/\tau}\right)$$

Thus, we have the solutin,

$$\langle r^2\rangle = v^2(0)\,\tau^2\left(1-e^{-t/\tau}\right)^2 - \frac{3kT}{M}\tau^2\left(1-e^{-t/\tau}\right)\left(3-e^{-t/\tau}\right) + \frac{6kT\tau}{M} + \cdots \quad (24)$$

Eqn (24) satisfies the initial conditions that both $\langle r^2\rangle$ and its first derivative vanishes at $t=0$.

Now, if we put $v^2(0) \approx 3kT/M$, it reduces to the solⁿ, i.e. eqn (7). Thus, we get the reversible nature of motion for $t \ll \tau$, with $\langle r^2\rangle \simeq v^2(0)t^2$ and, its irreversible nature for $t \gg \tau$ with

$$\langle r^2\rangle \simeq (6BkT)t.$$

The following figures show the variation of the ensemble averages $\langle v^2(t)\rangle$ and $\langle r^2(t)\rangle$ of a Brownian particle with time as given by eqn (23) and (24) respectively.

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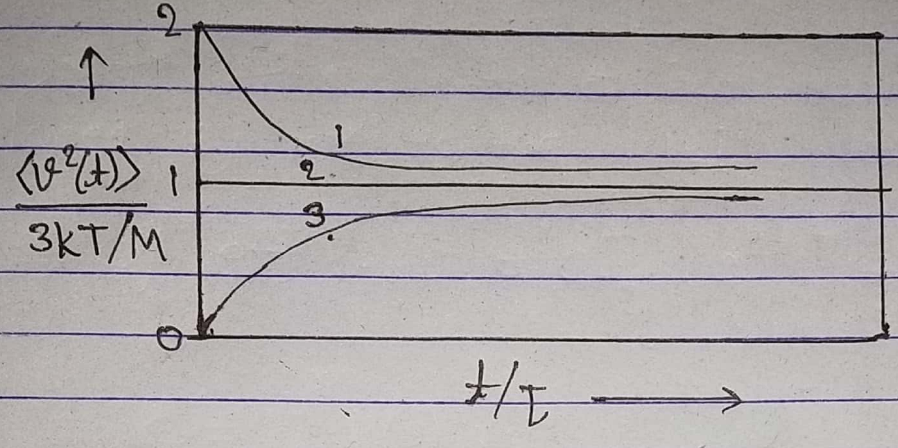

Fig (b)

The mean square velocity of a Brownian particle as a function of time. curves 1, 2, 3 correspond respectively to the ~~iniati~~ initial condions $v^2(0) = 6KT/M$, $3KT/M$ and 0.

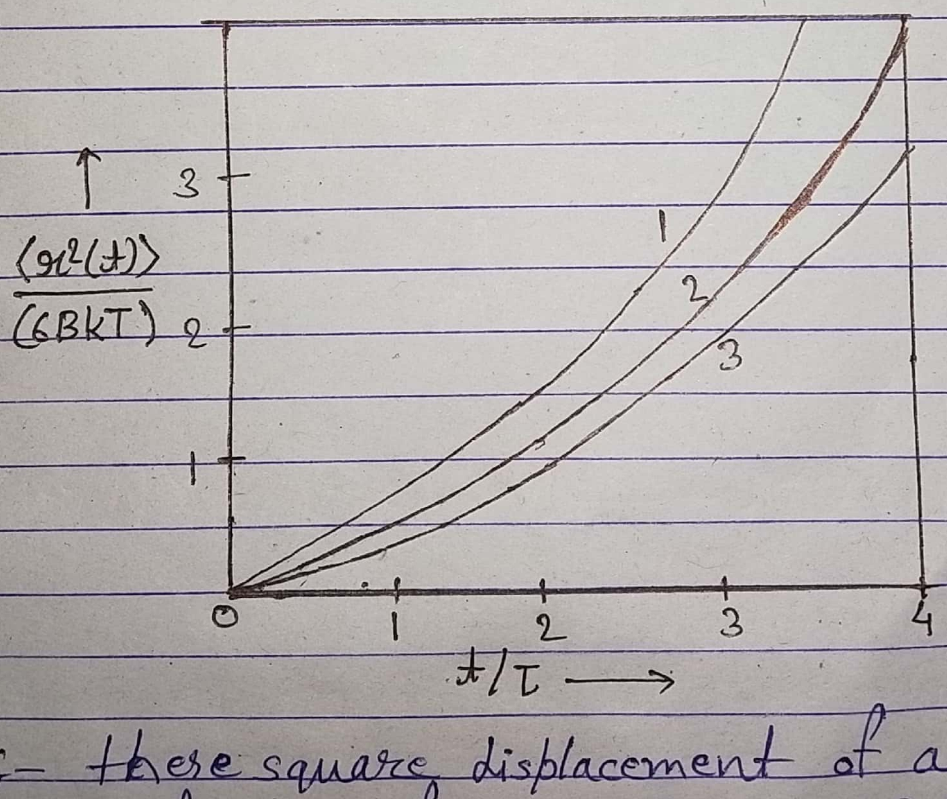

Fig (C)

Fig(C) ;- these square displacement of a Brownian particles as a function of time. Curves 1, 2, 3 corresponds respectively to the initial conditions $v^2(0) = 6KT/M$, $3KT/M$ and 0.