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Brownian Motion

This phenomenon was first observed by Brown in 1827 while examining the suspension of fine particles in water microscopically. It is found that these particles are moving rapidly and incessantly in an irregular fashion in all directions and each particle spins, sinks and rises again without ever coming to rest. This irregular motion is called Brownian motion.

Langevin's Theory of Brownian Motion :

Langevin's theory pf Brownian motion is based upon the fact that every particle of the suspension is bombarded from all sides by the liquid molecules. The number of collision is so large that it can not be distinct.

The effect of these collisions to produce systematic force which represent the dynamic friction or viscous force experienced by liquid particle and a fluctuating part of force responsible for Brownian motion.

According to Langevin, the force experienced by a suspended particle is of two kinds :

(*i*) Frictional force proportional to the velocity

$$f\left(\frac{dx}{dt}\right) = 6\pi\eta av$$

(*ii*) Force due to all external influences of the surrounding fluid.

Consider the motion of a particle in a specified direction say x – direction. The force on the particle is given by the equation.

$$m\left(\frac{d^2x}{dt^2}\right) = -f\left(\frac{dx}{dt}\right) + F \qquad ...(i)$$

Here, $-f\left(\frac{dx}{dt}\right)$ represents the component of the frictional force in the x – direction. F is the combined force due to other influences. Multiply equation (*i*) by x,

$$mx\left(\frac{d^2x}{dt^2}\right) = -fx\left(\frac{dx}{dt}\right) + Fx \qquad ...(ii)$$

Also $$\frac{d}{dt}(x^2) = 2x\left(\frac{dx}{dt}\right) \text{ and } x\left(\frac{dx}{dt}\right) = \frac{1}{2}\frac{d}{dt}(x^2)$$

$$\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right] = 2\left[x\left(\frac{d^2x}{dt^2}\right) + \left(\frac{dx}{dt}\right)^2\right]$$

$$\therefore \quad x\left(\frac{d^2x}{dt^2}\right) = \frac{1}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right] - \left(\frac{dx}{dt}\right)^2 \qquad ...(iii)$$

Substituting these values in equation (*ii*)

$$\frac{m}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right] - m\left(\frac{dx}{dt}\right)^2 = -\frac{f}{2}\frac{d}{dt}(x^2) + Fx \qquad ...(iv)$$

Equation (*iv*) represents the motion of a single particle. For all the particles, the mean value can be written as

$$\overline{\frac{m}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]} - x\overline{\left(\frac{dx}{dt}\right)^2} = \frac{f}{2}\overline{\frac{d}{dt}(x^2)} + \overline{Fx} \qquad ...(v)$$

As the force F varies completely in an irregular manner, it can be assumed that

$$\overline{Fx} = 0$$

Further, from the law of equipartition of velocities,

$$m\overline{\left(\frac{dx}{dt}\right)^2} = kT$$

$$\text{Also take } \frac{d}{dt}(x^2) = \frac{d}{dt}\left(\overline{x^2}\right) = U$$

Substituting these values in equation (v)

$$\frac{m}{2}\left(\frac{dU}{dt}\right) + \frac{fU}{2} = kT$$

or
$$\frac{dU}{dt} + \left(\frac{f}{m}\right)U = \frac{2kT}{m} \qquad ...(vi)$$

The general, solution of equation (vi) is

$$U = \frac{2kT}{f} + A\left[e^{-\left(\frac{f}{m}\right)t}\right] \qquad ...(vii)$$

As the value of m is very small, the value of (f/m) is very large and hence $e^{\left(\frac{-f}{m}\right)t}$ is negligibly small

$$\therefore \qquad u = \frac{2kT}{f} = \frac{d\overline{x^2}}{dt} \qquad ...(viii)$$

For a time interval $t = 0$ to $t = \tau$, integrating equation ($viii$), we get

$$\overline{x^2} - \overline{x_0^{\ 2}} = \left(\frac{2kT}{f}\right)\tau$$

At $t = 0$, $x_0 = 0$ and for small values, x^2 can be written as Δx^2

$$\therefore \qquad \overline{\Delta x^2} = \left(\frac{2kT}{f}\right)\tau \qquad ...(ix)$$

For each interval of time τ, the displacement Δx of the particle in the x – direction is determined. The mean square value $\overline{\Delta x^2}$ is calculated. In actual practice the particle makes millions of collisions and moves along zig-zag paths. The value $\overline{\Delta x^2}$ is only loosely related to the actual path.

According to Stokes's formula,

$$f\left(\frac{dx}{dt}\right) = 6\pi\eta a v = 6\,\pi\eta a\left(\frac{dx}{dt}\right)$$

$$\because \qquad f = 6\pi\eta a$$

$$\therefore \qquad \overline{\Delta x^2} = \frac{2kT\tau}{6\pi\eta a} = \frac{kT\tau}{3\,\pi\eta a} \qquad ...(x)$$

or
$$\left[\overline{\Delta x^2}\right]^{\frac{1}{2}} = \frac{(kT)^{\frac{1}{2}}\,(\tau)^{\frac{1}{2}}}{(3\pi\eta a)^{\frac{1}{2}}} \qquad ...(xi)$$

This theory indicates that $\overline{\Delta x^2}$ is not dependent on the mass of the particle. In the experiments of Perrin, the masses of the particles varied in the ratio 1 to 15000.

Further,

$$\left(\overline{\Delta x^2}\right)^{\frac{1}{2}} \propto \tau^{\frac{1}{2}}$$

and
$$\left(\overline{\Delta x^2}\right)^{\frac{1}{2}} \propto \frac{1}{\eta^{\frac{1}{2}}}$$

The effect of temperature is not very large because $\left(\Delta \overline{x^2}\right)^{\frac{1}{2}} \propto T^{\frac{1}{2}}$. However, viscosity decreases rapidly with increase in temperature. Thus, the pure temperature effect is negligibly small in comparison to the effect of viscosity.

Einstein's Theory of Brownian Motion

According to Einstein's theory of transitional Brownian motion, the particles tend to diffuse into the medium in course of time. Consequently, the diffusion coefficient must be related to the Brownian movement.

The diffusion coefficient can be calculated in two different ways :

(1) From the irregular motion of the suspended particles.

(2) From the difference in osmotic pressure caused by the differences in concentration of the suspended particles.

Calculation of Coefficient of diffusion from raindom molecular motion

Let D be the diffusion coefficient. Consider an imaginary cylinder with its axis along the x-axis. The end faces P and Q are separated by a distance Δ. Let n_1 and n_2 be molecular concentration at the end faces of the cylinder and A the area of cross-section.

The number of particles crossing the surface P to the right in time

$T = \frac{1}{2} n_1 \, A\Delta$

Similarly, the number of particles crossing the surface Q in the opposite direction $= \frac{1}{2} n_2 \, A\Delta$

It should be noted that half the particles contained in the imaginary cylinder move towards right whereas the other half move towards left.

The excess number of particles crossing a middle layer to the right $= \frac{1}{2}(n_1 - n_2)\, A\Delta$

From the definition of diffusion coefficient, the number,

$$\frac{1}{2}(n_1 - n_2)\, A\Delta = -D \frac{dn}{dx} \tau A$$

Here, $\left(\frac{dn}{dx}\right)$ is the concentration gradient.

But $$(n_1 - n_2) = -\Delta \frac{dn}{dx}$$

$$\therefore \quad -\frac{1}{2}\Delta^2 \left(\frac{dn}{dx}\right) = -D\left(\frac{dn}{dx}\right)\tau$$

$$\therefore \quad \Delta^2 = 2D\tau$$

or $$D = \frac{\Delta^2}{2\tau} \qquad ...(i)$$

Calculation of coefficient of diffusion from the difference in osmotic pressure :

If p_1 and p_2 are the osmotic pressures at the end P and Q, then from the gas laws

$$p_1 = n_1 kT$$
$$p_2 = n_2 kT$$

Thus the cylinder experiences a resultant force, $(p_1 - p_2)\,A = (n_1 - n_2)\,kTA$ along the +ve x - direction. This force is experienced by the particles contained in the cylinder.

The number of particles in the cylinder

$$= n\,A\,\Delta$$

where n is the mean concentration.

Therefore, the force acting on a single particle

$$f' = \frac{(n_1 - n_2)\,kTA}{nA\,\Delta} \qquad ...(ii)$$

Substituting the value of $(n_1 - n_2) = -\Delta\,\dfrac{dn}{dx}$ in equation (*ii*)

$$f' = -\left(\frac{dn}{dx}\right)\left(\frac{kT}{n}\right)$$

$$= 6\pi\eta a v$$

$$\therefore \qquad = -\left(\frac{kT}{n}\right)\left(\frac{dn}{dx}\right)$$

$$\text{or} \qquad nv = -\left(\frac{kT}{6\,\pi\eta a}\right)\left(\frac{dn}{dx}\right) \qquad ...(iii)$$

Here, nv is the number of particles moving to the right per unit area per second

$$\therefore \qquad nv = -D\left(\frac{dn}{dx}\right) \qquad ...(iv)$$

Equating (*iii*) and (*iv*)

$$-D\left(\frac{dn}{dx}\right) = -\left(\frac{kT}{6\pi\eta a}\right)\left(\frac{dn}{dx}\right)$$

$$\text{or} \qquad D = \left(\frac{kT}{6\pi\eta a}\right) = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta a}\right) \qquad ...(v)$$

From equations (*i*) and (*v*)

$$\frac{\Delta^2}{2\tau} = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta a}\right)$$

$$\Delta^2 = \frac{RT}{N}\left(\frac{1}{3\pi\eta a}\right)\tau \qquad ...(vi)$$

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