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Brownian motion on the basis of Langevin's theory.

Brownian Motion: — When a colloidal solution is examined under an ultramicroscope, the suspended particles in the solution look like bright illuminated spots. They appear like stars of light, moving to and fro, rapidly and continuously, in an entirely haphazard way. Each particle spins, rises, sinks and rises again. The motion is perpetual and spontaneous. This irregular motion is called the Brownian motion of the particles in the name of its observer Mr. Brown, a famous botanist.

This phenomenon gives a clear picture of the gaseous state of matter. The motion of the molecules of gas is similar in nature to the Brownian motion of suspended particles in colloidal solution.

Langevin's theory of Brownian motion

This theory is based on the hypothesis that the Brownian motion at right angles to gravity is entirely irregular. According to Langevin, every particle of the suspension is bombarded from all sides by the molecules of the liquid. The number of these collisions is so large that we cannot really speak of separate collisions.

There is about 10^{21} collision per second suffered by a brownian particle in a liquid under normal condition and each collision is expected to produce a link in the path of the particle. Let us assume that the effect of these collisions to produce an average systematic force representing the dynamic friction or viscous force experienced by the particle and a fluctuating part F of the force which is responsible for Brownian motion. Assuming the particles to be spherical; the viscous force f along any arbitrarily chosen axis x is thus given by.

$$f = -6\pi\eta r v = -c \frac{dx}{dt}$$

where $v = \frac{dx}{dt}$ is the velocity of the particle, r its radius and $c = 6\pi\eta r$. The equation of motion for the particle is thus given by

$$m \frac{d^2x}{dt^2} = -c \frac{dx}{dt} + F \quad \text{--- (1)}$$

The particle suffers collision every instant with the molecules of the liquid and hence its motion is changed in direction. Multiplying equation (1) by x , we have

$$m x \left(\frac{d^2x}{dt^2} \right) = -c x \left(\frac{dx}{dt} \right) + F x \quad \text{--- (2)}$$

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

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

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

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

$$\therefore x \left(\frac{d^2x}{dt^2} \right) = \frac{1}{2} \frac{d}{dt} \left[\frac{d}{dt} (x^2) \right] - \left(\frac{dx}{dt} \right)^2 \quad \text{--- (3)}$$

Substituting these value in equation (2)

$$\frac{m}{2} \frac{d}{dt} \left[\frac{d}{dt} (x^2) \right] - m \left(\frac{dx}{dt} \right)^2 = -\frac{c}{2} \frac{d}{dt} (x^2) + Fx \quad \text{--- (4)}$$

This equation represent the motion of a single particle.

Integrating this equation with respect to time between the limits $t=0$ to $t=t$

$$\frac{m}{2} \int_0^t \frac{d}{dt} \left[\frac{d}{dt} (x^2) \right] dt - m \int_0^t \left(\frac{dx}{dt} \right)^2 dt = -\frac{c}{2} \int_0^t \frac{d}{dt} (x^2) dt + \int_0^t Fx dt$$

$$\text{or, } \frac{m}{2} \left[2x \frac{dx}{dt} \int_0^t dt \right] - m \int_0^t \left(\frac{dx}{dt} \right)^2 dt = -\frac{c}{2} \left[x^2 \right]_0^t + \int_0^t Fx dt$$

The first term is negligible in comparison to the second term since x varies as \sqrt{t} for random motion and $\left(\frac{dx}{dt} \right)$ varies quite irregularly ~~with~~ with time due to collisions with the molecule of the liquid. The second term increases with t because $\left(\frac{dx}{dt} \right)^2$ will have some average value in course of time. The last term is not negligible due to the randomness of F and the steady increase of x ~~so~~ it varies faster than \sqrt{t} .

The last term containing F disappears, because it is positive for some particle and negative for other. Since the particles are in

thermal equilibrium, their mean kinetic energy must be given by the equipartition law. Hence the mean kinetic energy for one degree of freedom.

$$\frac{1}{2} m \left(\frac{dx}{dt} \right)^2 = \frac{1}{2} kT$$

Therefore averaging over a large number of particles we, get,

$$m \overline{\int_0^t \left(\frac{dx}{dt} \right)^2 dt} = \int_0^t m \left(\frac{dx}{dt} \right)^2 dt = kTt$$

The bar denotes the average over particles.

∴ From equation (5), we get

$$kTt = \frac{1}{2} c \overline{\Delta(x^2)}$$

where $\Delta(x^2)$ denotes the change in x^2 in time t . Assuming the particles to start from origin we have

$$\Delta(x^2) = x^2 \quad \therefore \overline{x^2} = \left(\frac{2kT}{c} \right) t \quad \text{--- (6)}$$

According to Stokes's formula

$$c \left(\frac{dx}{dt} \right) = 6\pi\eta r v = 6\pi\eta r \left(\frac{dx}{dt} \right)$$

$$\therefore c = 6\pi\eta r$$

∴ From equation (6)

$$\overline{(x^2)} = \left(\frac{kT}{3\pi\eta r} \right) t \quad \text{--- (7)}$$

where τ is interval of time sufficiently large to allow a large number of collision to have taken place.

If we denote the components of the displacement of the particle along the x -axis by Δx in place of x , we have

$$\overline{(\Delta x)^2} = \left(\frac{kT}{3\pi\eta r} \right) \tau = \frac{RT}{N} \cdot \frac{1}{3\pi\eta r} \cdot \tau \quad \text{--- (8)}$$

This theory indicates that $\overline{(\Delta x)^2}$ is independent of the mass of the particle.

In the experiment of Perrin, the masses of particles varied in the ratio 1 to 15000. However, within the limits of experimental error, the value of Boltzmann's constant k is the same.

$$\text{Further } \overline{(\Delta x)^2} \propto \tau \propto \frac{1}{\eta}$$

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