The Theory of Brownian Motion

(Einstein, von Smoluchowski, Langevin)

1/. Pollen grains suspended in water show random zig-zig movement (Robert Brown).

2/. Light molecules of large size, or large molecular aggregates such as Colloids, also show Brownian motion.

Discrete molecular view

3/. This motion happens due to random non-uniform impact of neighbouring molecules of the solution, on a large particle, at a given instant in time.

4/. At any instant the particle is acted on by a net unbalanced force that has a random direction.

5/. The force opposing this motion is the viscous drag of the liquid.

Continuum view

6/. Particles of size 6nm (6×10^{-9}m) can be followed in their Brownian motion (under an ultramicroscope).

Assumption: Mean kinetic energy of a suspended particle is the same as that of a gas molecule at the same temperature. (Thermalisation)

For an ideal gas $\boxed{PV = nRT}$ and the mean (average) kinetic energy of the molecules is

$$\boxed{\langle \mathcal{E}_K \rangle = \langle \tfrac{1}{2} m v^2 \rangle = \tfrac{3}{2} k_B T}$$

(due to the Equipartition Theorem). Here $\boxed{k_B = R/N_A}$

$k_B \rightarrow$ Boltzmann's constant, $N_A \rightarrow$ Avogadro's number.

For one-dimensional motion, along the x-direction only, $\boxed{\langle \mathcal{E}_K \rangle = \tfrac{1}{2} k_B T = \langle \tfrac{1}{2} m v_x^2 \rangle}$

$$\Rightarrow \boxed{\left\langle \frac{1}{2} m v_x^2 \right\rangle = \frac{1}{2} \frac{RT}{N_A}}$$

(ONLY for one-dimensional motion.)

The Equation of the Motion in One-Dimension

1. Along the x-direction, the particle is acted upon by a random force, X, which drives the particle.
2. This force is opposed by a retarding force due to the viscous drag of the liquid.

Stokes's Law and the Viscous Drag

$W \to$ Weight, $B \to$ Buoyancy

For a heavy spherical particle falling through a long column of liquid,

$\boxed{m\frac{dv}{dt} = (W-B) - \delta v}$ where $\boxed{\delta = 6\pi\eta a}$

$\eta \to$ Viscosity coefficient; $a \to$ radius of sphere.

Viscous drag $\propto$ velocity (in liquids).

$\therefore$ The equation of the motion of a single particle experiencing these two forces is

$$\boxed{m\frac{d^2x}{dt^2} = X - \delta\frac{dx}{dt}}$$ (X is a random force).

Due to random bombardment the particle can go either in the $+x$ or the $-x$ directions, whose average displacement will be zero. ($\langle x\rangle = 0$).

Just to extract the magnitude of the displacement (a vector), we need to set up an equation in x^2. Hence,

$$\boxed{m x\frac{d^2x}{dt^2} + \delta x\frac{dx}{dt} = xX}$$. Multiplying throughout by x.

The first Term: $\boxed{x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2x^2}{dt^2} - \left(\frac{dx}{dt}\right)^2}$

Check: $\frac{1}{2}\frac{d^2x^2}{dt^2} = \frac{1}{2}\frac{d}{dt}\left[\frac{d(x^2)}{dt}\right] = \frac{1}{2}\frac{d}{dt}\left(2x\frac{dx}{dt}\right)$

$\therefore \frac{1}{2}\frac{d^2x^2}{dt^2} = \left(\frac{dx}{dt}\right)^2 + x\frac{d^2x}{dt^2}$ (used in the first term)

Now, $\boxed{x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d}{dt}\left[\frac{d(x^2)}{dt}\right] - \left(\frac{dx}{dt}\right)^2}$

The Second Term: $\boxed{\delta x\frac{dx}{dt} = \frac{\delta}{2}\frac{d(x^2)}{dt}}$

Recasting the Equation of Motion as,

$$\boxed{\frac{m}{2}\frac{d}{dt}\left[\frac{d(x^2)}{dt}\right] - m\left(\frac{dx}{dt}\right)^2 + \frac{\delta}{2}\frac{d(x^2)}{dt} = xX}.$$

The foregoing equation is applied to a large number of particles of the same size (such as pollen or colloids), and the average is taken. This gives $\langle xX\rangle = 0$, because both X and x are random.

Further, $\boxed{\left\langle m\left(\frac{dx}{dt}\right)^2\right\rangle = m\left\langle\left(\frac{dx}{dt}\right)^2\right\rangle = m\langle v_x^2\rangle}.$

But $\boxed{m\langle v_x^2\rangle = \frac{RT}{N_A}}$ (From the kinetic theory and the Equipartition Theorem)

$\boxed{k_B = R/N_A}$

Now we define $\boxed{\alpha = \left\langle \frac{d(x^2)}{dt} \right\rangle}$ to get,

$$\boxed{\frac{m}{2}\frac{d\alpha}{dt} - \frac{RT}{N_A} + \frac{\delta\alpha}{2} = 0}$$ (The average equation)

$$\Rightarrow \boxed{\frac{m}{\delta}\frac{d\alpha}{dt} = \frac{2RT}{\delta N_A} - \alpha}$$

$$\Rightarrow \frac{d\alpha}{d(\delta t/m)} = \frac{2RT}{\delta N_A} - \alpha .$$

$\alpha \equiv \alpha(t)$

We rescale t as $\boxed{\tau = \delta t/m}$ and get

$$\boxed{\frac{d\alpha}{d\tau} = -\left(\alpha - \frac{2RT}{\delta N_A}\right)}$$

m/δ has the physical dimension of time.

$$\Rightarrow \int \frac{d\alpha}{\alpha - (2RT/\delta N_A)} = -\int d\tau$$

$$\Rightarrow \ln\left(\alpha - \frac{2RT}{\delta N_A}\right) = -\tau + \ln A$$

($A \to$ integration constant)

$$\Rightarrow \boxed{\alpha = \frac{2RT}{\delta N_A} + A e^{-\delta t/m}} .$$

From Stokes' Law $\boxed{\delta = 6\pi\eta a}$ (assuming that the particles are like rigid spheres of mass m). Now $\boxed{m = \rho \frac{4}{3}\pi a^3}$, in which ρ is the average density of the spherical particles.

$$\therefore \boxed{\frac{\delta}{m} = \frac{6\pi\eta a}{\rho\frac{4}{3}\pi a^3} \sim \frac{\eta}{\rho a^2}}$$

Take $\eta \sim 0.01$ cgs. for water

Standard values in the c.g.s. system ($\eta \approx \underset{\text{(air)}}{0.0001} - \underset{\text{(water)}}{0.01}$ c.g.s unit, $a \sim 10^{-4}$ cm etc.), render $\boxed{\frac{\delta}{m} \sim 10^5 - 10^6}$. Standard time intervals between collisions is $\boxed{10^{-4}\,s}$. Hence $\boxed{\frac{\delta}{m}t \sim 100}$. $\therefore$ $\boxed{e^{-100} \text{ is negligible}}$.

Hence we write $\boxed{\alpha \simeq \frac{2RT}{\delta N_A}}$.

Now $\boxed{\alpha = \left\langle \frac{d}{dt}(x^2) \right\rangle = \frac{d}{dt}\langle x^2 \rangle}$ Exchanging differential operators and summation.

$$\Rightarrow \boxed{\frac{d}{dt}\langle x^2 \rangle \simeq \frac{2RT}{\delta N_A}}$$ → The right hand side is a constant.

$\boxed{k_B = R/N_A}$

$$\Rightarrow \boxed{\langle x^2 \rangle \simeq \left(\frac{2RT}{\delta N_A}\right)t}$$ or $\boxed{\langle x^2 \rangle \propto t}$.

$$\boxed{\frac{RT}{\delta N_A} = \left(\frac{k_B T}{6\pi\eta a}\right)}$$

Write $\boxed{D = \frac{k_B T}{\delta}}$

$$\Rightarrow \boxed{\langle x^2 \rangle = 2Dt}$$

(Einstein - Smoluchowski Equation)

$\boxed{\delta = \frac{k_B T}{\delta} \text{ (Einstein relation)}, \; D = \frac{k_B T}{6\pi\eta a} \text{ (Einstein-Stokes Equation)}}$

The Brownian motion is a random process in which $\boxed{\langle x \rangle = 0}$ and $\boxed{\langle x^2 \rangle = 2Dt}$.

Norbert Wiener

The Wiener Process

In the Random Walk: $\boxed{\langle m \rangle = (p-q)N}$ and $\boxed{\langle x \rangle = \langle m \rangle l}$.

In the Continuous Limit of Probability Distribution: $\boxed{P(x) = \frac{1}{\sqrt{2\pi}\,\sigma} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right]}$

$\boxed{\mu = Nl(p-q)} \Rightarrow \mu = \langle m \rangle l \Rightarrow \boxed{\mu = \langle x \rangle}$. (The Mean)

$\boxed{\sigma^2 = 4l^2 Npq} \Rightarrow \boxed{\sigma^2 = l^2 \langle (\Delta m)^2 \rangle = l^2 \left[\langle m^2 \rangle - \langle m \rangle^2\right]}$.

Now $\langle (\Delta m)^2 l^2 \rangle = \langle m^2 l^2 \rangle - \langle ml \rangle^2$.

Since $\boxed{x = ml} \Rightarrow \boxed{\langle (\Delta x)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2}$

(The Variance is an example of dispersion)

$\Rightarrow \boxed{\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2}$ (Variance)

$\boxed{\sigma^2 = \langle x^2 \rangle}$ when $\boxed{\langle x \rangle = 0}$ (for $p = q$)

When $\boxed{\langle x^2 \rangle = 2Dt}$ $\Rightarrow$ σ (standard deviation) is $\boxed{\sigma \propto t^{1/2}}$ (Wiener Process)

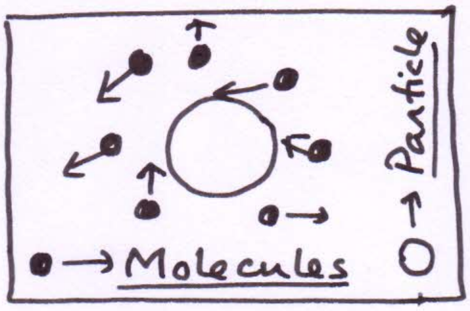
(for $\boxed{\mu = 0}$).

Examples are the Point-Source Solution of the diffusion equation and Brownian motion.

> In the Continuous Limit the Equivalence between the Random Walk and the Gaussian Profile is held fully (with infinite samplesize)
>
> A stochastic process with zero mean and a linear time-dependent variance is a Wiener Process.

Brownian Motion: Additional Remarks

1/. A large particle suspended among randomly moving molecules, is pushed around randomly by a net unbalanced instantaneous force due to the molecules.



2/. When considering the random impact of the molecules, a discrete granular view of the liquid is taken. But when considering the viscous drag, the liquid is viewed as a fluid continuum.

3/. Although the large isolated particle is suspended in a liquid, its average kinetic energy is thermalised with gas molecules at the same temperature as the liquid. => $\boxed{\text{Kinetic energy} \sim k_B T}$

4/. Degrees of Freedom: In a large aggregate of particles (which is described statistically), the degree of freedom refers to the number of squared terms contributing to the energy.

(P.T.O.)

4/. **Example**: i) A single atom in an ideal gas, with no potential energy but only kinetic energy, can move in three directions, x, y, z. Hence, its kinetic energy $\boxed{\mathcal{E}_k = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}$.
Since there are three quadratic terms, (v_x^2, v_y^2, v_z^2), the number of degrees of freedom is three.

Example: ii) A particle on a spring, moving only along the x-direction, has total energy $\boxed{\mathcal{E} = \frac{1}{2}mv_x^2 + \frac{1}{2}kx^2}$. There are two quadratic terms (v_x^2, x^2), and so the number of degrees of freedom is two.

5/. The Equipartition Theorem: In thermal equilibrium, on average, the total energy is equally partitioned (shared) among all the degrees of freedom. Each degree of freedom has energy $\boxed{\frac{1}{2}k_B T}$.

6/. Stokes's Law and Viscous Drag:

$$\boxed{m\frac{dv}{dt} = W(\text{weight})\downarrow - B(\text{Buoyancy})\uparrow - \delta v\uparrow \left(\begin{matrix}\text{Viscous}\\ \text{Drag}\end{matrix}\right)}$$

For a sphere $\boxed{\delta = 6\pi\eta a}$ → The viscous drag coefficient, which depends on the viscosity η and the radius a. Clearly δ increases for both increasing η and a (larger objects encounter greater resistance)

Buoyancy → Upthrust → Weight of liquid displaced.

7/. Averaging requires summation (integration).

Hence $\boxed{\left\langle \frac{d}{dt}(x^2)\right\rangle = \frac{d}{dt}\langle x^2\rangle}$ the order of the differentiation and the integration (summation) does not matter. The two operations can be exchanged.

8/. In the c.g.s system of unit, the viscosity coefficient $\boxed{\eta \sim 10^{-4}\,\text{unit (air)} - 10^{-2}\,\text{unit (water)}}$.

For Brownian motion in water, the latter value is taken, which gives $\boxed{\frac{\delta}{m} \sim 10^{6}\,(\text{unit})} \to s^{-1}$

9/. The relevant time scale is the time between successive collisions $\sim \boxed{10^{-4}\,s}$