Brownian Motion

Discovered in 1827 by Robert Brown while studying pollen grains. Reported with inorganic particles to show motion is physical in nature, not biological.

Cause of Brownian motion is the momentary imbalance of molecular collision forces, which causes "random walk" behavior.

As shown by Einstein, Brownian motion is a consequence of the "equi-partition" principle of statistical mechanics where all species in a mixture have an average kinetic energy given by

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

Consider random walk behavior in 1D (since x, y, z directions are independent).

An elementary statistical result:

Let moments be $\Delta y_1$, $\Delta y_2$, $\Delta y_3$ etc. (e.g. $\Delta y_1 = +\Delta y$, $\Delta y_2 = -\Delta y$, $\Delta y_3 = -\Delta y$)

$$R^2 = (\Delta y_1 + \Delta y_2 + \Delta y_3 + \cdots)^2 = (\Delta y_1 + \Delta y_2 + \Delta y_3 + \cdots)(\Delta y_1 + \Delta y_2 + \Delta y_3 + \cdots)$$

$$= \Delta y_1^2 + \Delta y_2^2 + \Delta y_3^2 + \cdots + 2 \Delta y_1 \Delta y_2 + 2 \Delta y_1 \Delta y_3 + \cdots$$

Since $\Delta y_1$, $\Delta y_2$ etc. are randomly negative or positive,

For a large number of steps (N) first sum dominates

$$(R^2)_{\text{ave}} = N \langle (\Delta y_1)^2 \rangle$$

Note: $\langle (\Delta y_1)^2 \rangle = \langle \Delta y^2 \rangle$
\[(R^2)_{\text{ave}} = \frac{\sigma_y^2}{1} \text{ where experiment with } N \text{ steps is repeated many times}\]

By analogy, in a single experiment with \(N\) steps, there is a probability the particle will be at a given location \(N_2 > N_1\).

Define the "Mean Square displacement" for an experiment with \(N\) steps as:

\[\overline{y^2} = \sum_{y=-\infty}^{\infty} y^2 \cdot P(y)\]

It follows that \((R^2)_{\text{ave}} = \overline{y^2} = N \cdot (\Delta y)^2\)

Since \(P(y)\) can also be interpreted as being proportional to the number of experiments yielding the final position \(y\) if the experiment with \(N\) steps is repeated many times.

Can also think in terms of a collection of particles released at \(y=0\) at \(t=0\).

Particle concentration is thus proportional to \(P(y)\):\n
\[\frac{\sigma_y^2}{1} = \text{number of steps} \quad \text{or} \quad N = \frac{t}{\Delta t}\]

\[\text{total mass} \rightarrow N\]

\[\Delta y \rightarrow \Delta t\]
Consider next the work of Albert Einstein
Two publications of interest:


Molecules undergo a random jump of \( \pm \delta y \) in the time period \( dt \)

On the time period \( dt \) the number of molecules jumping from left to right across \( E \) is \( \frac{1}{2} \) \( C_{L} \delta y \), and from right to left is \( \frac{1}{2} \) \( C_{R} \delta y \). The flux across \( E \) is therefore

\[
J = \frac{1}{2} \delta y (C_{L} - C_{R}) A
\]

\[
A \frac{dt}{dy}
\]

\( C_{L} \) is the average concentration of the left compartment = \( C(A \frac{dy}{2}) \), and similarly \( C_{R} = C(A \frac{dy}{2}) \) so

\[
J = \frac{1}{2} \delta y (C(A - \frac{dy}{2}) - C(A + \frac{dy}{2})) \delta y = \frac{1}{2} \delta y^{2} \frac{dc}{dt} \delta y
\]
This is Fick's Law with \( D = \frac{1}{2} \frac{\Delta y^2}{\Delta t} \)

Combine with \( \overline{y^2} = N (\Delta y)^2 \) noting that \( N = \frac{t}{\Delta t} \) yields:

\[
\overline{y^2} = 2D \Delta t \quad \text{and} \quad (\overline{y^2})^{\frac{1}{2}} = \sqrt{2D \Delta t}
\]

Recall the case of diffusion from an infinitesimal slice yields \( C(x) \)

\[
(\overline{y^2})^{\frac{1}{2}} = \frac{4}{N} \sqrt{D \Delta t}
\]

Consider next the van't Hoff law

[Named after Jocuines van't Hoff (1901 Nobel Prize)]

"Equilibrium" Osmotic pressure:

\[
\frac{\partial M}{\partial P} = \overline{\Delta W} \to \text{Rasington correction}
\]

\[
M'_W = M^0_W + RT \ln X_W + \overline{\Delta W} \Delta T
\]

but \( \ln X_W = \ln (1 - x_A) \approx -\frac{x_A}{W} \)

\[
\overline{\Delta W} \approx \frac{-CA}{W} \overline{CA_W}
\]

Setting \( M_W = M''_W \)

\[
\Delta T = \frac{RTCA}{\overline{\Delta W}} \quad \text{inherent gas constant}
\]

Also

\[
\Delta T = RT(C_A' - C''_A) \quad \text{if \( C_A'' \neq 0 \)}
\]
Einstein noted that the van't Hoff applies regardless of the size of the solute and it therefore applies to the case of particles.

Consider the following thought experiment for 1D diffusion:

**Face needed to keep membrane in place and to therefore “stop” diffusion**

F = A ΔT = ART ΔC_A

**Force per unit volume of fluid**:

\[
\frac{F}{A L} = \frac{ART}{\mathcal{A}} \frac{dc_A}{dx} = RT \frac{dc_A}{dy}
\]

**Face per mole**

\[
\frac{F}{A L C_A} = \frac{RT d\ln C_A}{C_A \frac{dy}{dx}} = \frac{RT d\ln C_A}{dy}
\]

When A is dilute,

\[
\frac{d\ln C_A}{dy} \approx \frac{d\ln x_A}{dy}
\]

\[
RT d\ln C_A = -\frac{d}{dy} \mu_A = -\nabla \mu_A
\]

This must also be the force that causes diffusion if the membranes are removed. When membranes are removed, this force will cause an acceleration up to the terminal velocity where drag force balances the propulsion force.
Stokes Law:

\[ U = \frac{F'}{6\pi \mu R_A} \quad \text{free on one molecule} \]

\[ F' = F_N \frac{RT}{N Av} \frac{1}{C_A} \frac{dC_A}{dy} \]

\[ U = \frac{RT}{6\pi \mu R_A N Av C_A} \frac{dC_A}{dy} \]

Since \( C_A \cdot U = J_A = \text{flux of } A \):

\[ J_A = \frac{RT}{6\pi \mu R_A N Av} \frac{dC_A}{dy} \]

\[ D_A \]

Note that \( R \) is known from \( P-V-T \) experiments with "ideal" gases:

Combine "Charles" law and "Boyle's" law:

\[ PV = \text{const.} \times T \quad \text{(constant for different gases)} \]

Combine with "Avogadro Principle" ("Equal volumes of all gases at the same temperature and pressure contain the same number of molecules")

\[ PV = n \frac{RT}{k} \quad \text{"Universal" gas constant} \]

\[ n \text{ number of "molecules"} \]
In 1860, Stanislaw Carnigaro standardized the atomic weight scale by setting the molecular weight of O₂ at 16, so that 1 mole became defined as the number of molecules in 16 grams of O₂. But this number, which became known as "Avogadro's number," was itself unknown. However, since \( R \) can be determined by measuring \( P, V, T \) for a known mass of O₂, Brownian motion experiments can be used to determine \( N_A = \frac{2 \times RT}{6\sqrt{\pi} \cdot M \cdot \text{Avogadro}} \).

\[
\overline{y^2} = \frac{2RI}{6\sqrt{\pi} \cdot M \cdot \text{Avogadro}}
\]

keep track of the times the particle is at various locations to measure probability function \( P(y) \), then determine \( \overline{y^2} = \sum_{i=1}^{\infty} y_i^2 / (\tfrac{\partial^2}{\partial t^2}) \).

Experimental, if a particle location is determined at the time \( t_0 \), then at any time \( \overline{y^2} = \sum_{i=1}^{\infty} y_i^2 / (\tfrac{\partial^2}{\partial t^2}) \) where \( y_i \) is the particle location at the \( i \)th time step.

Jean Perrin performed the experiment in 1906 and determined that \( N_A = 6.5 - 6.9 \times 10^{23} \). The size of molecules can also now be estimated. For liquid water 18 grams (1 mole) occupies 18 mL so \( D = \sqrt[3]{0.018 \text{ cm}^3 / 1000 \text{ cm}^3 / \text{mole} / \text{Avogadro} \cdot 10^{23} \text{ Å} = 3 \text{ Å} \).
In the early 1900's, the existence of molecules was not accepted by all scientists (e.g., Wilhelm Ostwald and Ernest Mach). Brownian motion experiments and their explanation by Einstein, was considered the "smoking gun" that proved molecules exist.

Since Fick's Law follows from Brownian motion analysis, any time dependent diffusion process is described by \( \overline{y^2} = 2D\Delta t \).

**Example:**

\[ \text{at } t=0 \text{ M molecules are present at } y=0. \]

\[ C = \text{molecules per unit width in y direction} \]

\[ M \]

\[ \text{need to solve } \frac{\partial C}{\partial t} = 0 \frac{\partial^2 C}{\partial y^2} \]

\[ \text{subject to } \int_{-\infty}^{\infty} C \, dy = M \]

\[ \text{Solution is } C = \frac{M}{\sqrt{2\pi D t}} \exp \left( -\frac{y^2}{4Dt} \right) \]

\[ \text{calculate } \overline{y^2} : \]

\[ \overline{y^2} = \int_{-\infty}^{\infty} y^2 C \, dy / M \]

\[ = \frac{1}{2\pi D t} \int_{-\infty}^{\infty} y^2 \exp \left( -\frac{y^2}{4Dt} \right) \, dy \]

\[ = 2D\Delta t \]
Relation between Nernst–Einstein Equation and the Boltzmann Relation:

Particles suspended in liquid under gravitational force.

\[ \frac{u_A}{F_A} \text{ number density} \]

\[ N_A = \text{mobility}_A \cdot F_A \cdot C_A - D_A \frac{dC_A}{dz} \]

At steady state, \( N_A = 0 \). Also \( F_A = -m_A \frac{g}{l} \)

Substituting:

\[ 0 = \text{mobility}_A (-m_A) \frac{g}{l} C_A - D_A \frac{dC_A}{dz} \]

So that

\[ -\text{mobility}_A m_A \frac{g}{l} \frac{dz}{D_A} = \frac{dC_A}{C_A} \]

Integrating from \( z = 0 \) (where \( C_A = C_{A,0} \)) to \( z \)

\[ -\text{mobility}_A m_A \frac{g}{l} \frac{z}{D_A} = \ln \frac{C_A}{C_{A,0}} \]

So that

\[ C_A = C_{A,0} \exp \left( -\frac{m_A \frac{g}{l} z}{D_A / \text{mobility}_A} \right) \]

But \( m_A \frac{g}{l} z \) is the gravitational potential energy. So above relation is equivalent to Boltzmann relation \( \beta \rightarrow D_A / \text{mobility}_A = kT \)