

Brownian Motion

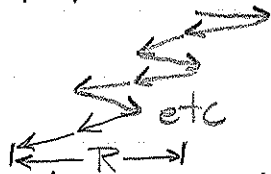
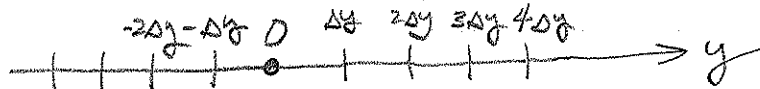
Discovered in 1827 by Robert Brown while studying pollen grains. Repeated with inorganic particles to show motion is physical in nature, not biological.

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)



movement determined by flipping a coin (heads = left; tails = right)

An elementary statistical result:

Let movements be $\Delta y_1, \Delta y_2, \Delta y_3$ etc.

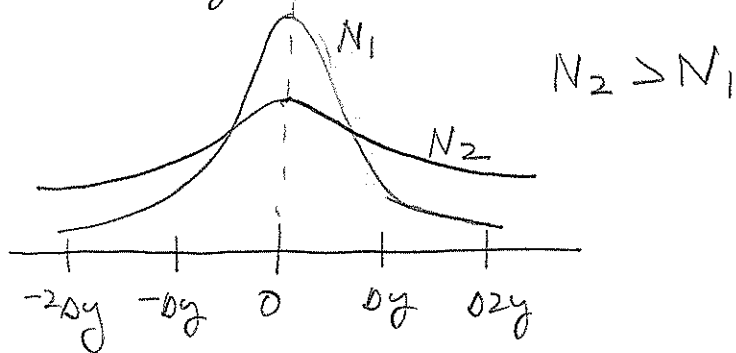
(Eg. $\Delta y_1 = +\Delta y, \Delta y_2 = -\Delta y, \Delta y_3 = -\Delta y$)

$$\begin{aligned}
 R^2 &= (\Delta y_1 + \Delta y_2 + \Delta y_3 + \dots)^2 \\
 &= (\Delta y_1 + \Delta y_2 + \Delta y_3 + \dots) * (\Delta y_1 + \Delta y_2 + \Delta y_3 + \dots) \\
 &= \underbrace{\Delta y_1^2 + \Delta y_2^2 + \Delta y_3^2 + \dots}_{N(\Delta y)^2} + \underbrace{2\Delta y_1\Delta y_2 + 2\Delta y_2\Delta y_3 + \dots}_{\text{random value}}
 \end{aligned}$$

Since $\Delta y_1, \Delta y_2$ etc. are randomly negative or positive, for large number of steps (N) first sum dominates $(R^2)_{ave} = N(\Delta y)^2$, Note: $(-\Delta y)^2 = (\Delta y)^2$

$(R^2)_{ave}$ = average value of R^2 where R is expected many times
 where experiment with N steps is repeated many times
 $|\Delta y|$ = magnitude of step size

By analogy, for a single experiment with N steps, there is a probability the particle will be at a given location



Define the "mean square displacement" for an experiment with N steps

$$\overline{y^2} = \int_{-\infty}^{\infty} y^2 P(y) dy$$

← $P(y)$ is the probability that particle is located at y

It follows that $(R^2)_{ave} = \overline{y^2} = N (\Delta y)^2$
 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 then proportional to $P(y)$

each particle undergoes same number of steps
 Δt is time for a step of Δy so $N = t/\Delta t$

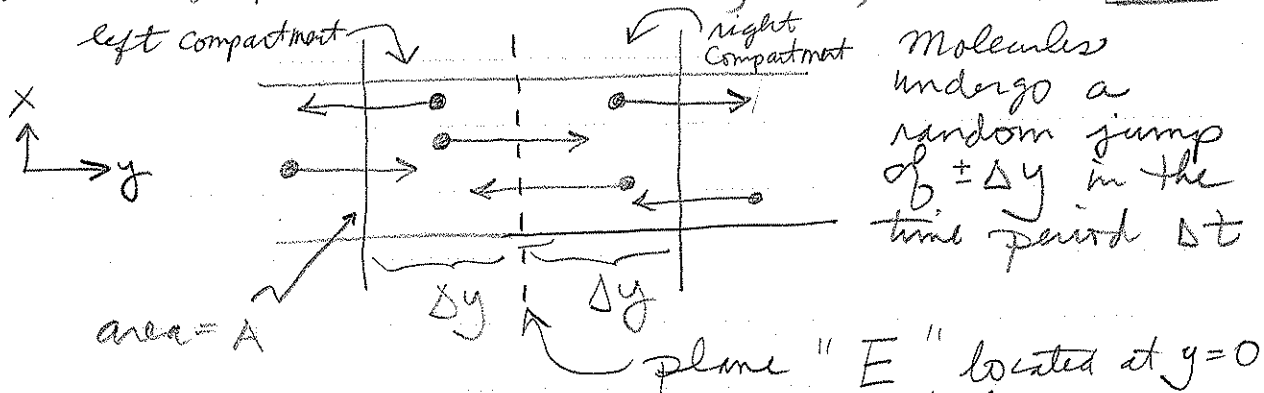
$$\overline{y^2} = \int_{-\infty}^{\infty} y^2 C(y) dy$$

total moles present $\rightarrow M$
 C = amount present per unit width in y direction

Consider next the work of Albert Einstein
Two publications of interest:

"On the movement of small particles
suspended in a stationary liquid
demanded by the molecular-kinetic
theory of heat," *Annalen der Physik*, 17, 549, 1905.

"Elementary theory of Brownian Motion"
Zeit. für Electrochemie, 14, 235, 1908.



In the time period Δt the ^{number of} moles jumping from left to right across E is $\frac{1}{2} C_{\text{left}} A \Delta y$, and from right to left is $\frac{1}{2} C_{\text{right}} A \Delta y$. The flux across E is therefore

$$J = \frac{\frac{1}{2} \Delta y (C_{\text{left}} - C_{\text{right}}) A}{A \Delta t}$$

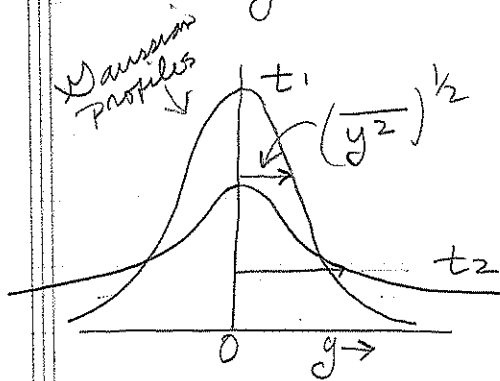
C_{left} is the average concentration of the left compartment = $C(-\frac{\Delta y}{2})$, and similarly $C_{\text{right}} = C(\frac{\Delta y}{2})$ so

$$J = \frac{\frac{1}{2} \Delta y (C(-\frac{\Delta y}{2}) - C(\frac{\Delta y}{2}))}{\Delta t \Delta y} = -\frac{1}{2} \frac{\Delta y^2}{\Delta t} \frac{dC}{dy}$$

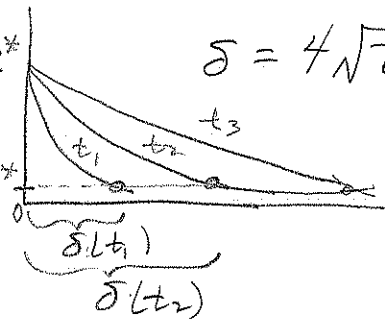
This is Fick's Law with $D = \frac{1}{2} \frac{\Delta y^2}{\Delta t}$

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

$$\overline{y^2} = 2 D t \quad \text{or} \quad (\overline{y^2})^{1/2} = \sqrt{2 D t}$$

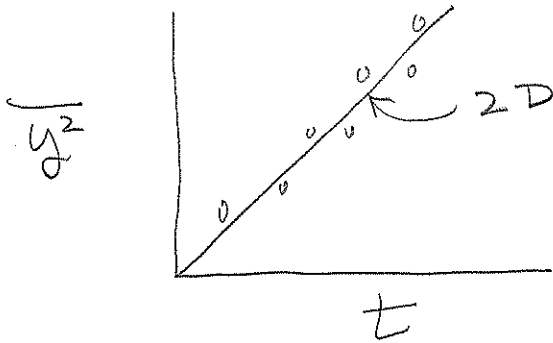


recall the case of diffusion from an interface, dc/dx at fixed C^*

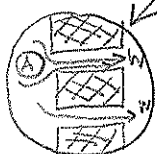
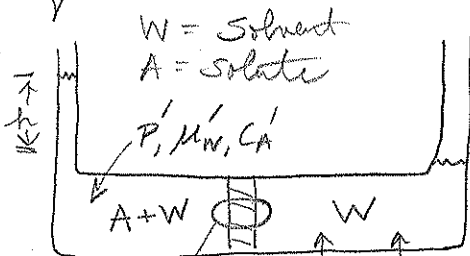


Standard deviation of concentration profiles

$$\delta = 4 \sqrt{D t}$$



Consider next the van't Hoff Law
 [Named after Jacobus van't Hoff (1901 Nobel Prize)]
 "Equilibrium" Osmotic pressure:



$\mu_w'' = \mu_w^0$
 $P g h = P' - P'' = \Delta \Pi$
 Osmotic Pressure

$\frac{\partial \mu_w}{\partial P} = \bar{V}_w \rightarrow$ Poynting correction

$$\mu_w' = \mu_w^0 + RT \ln X_w + \bar{V}_w \Delta \Pi$$

but $\ln X_w = \ln(1 - X_A) \approx -X_A \approx -\frac{C_A \bar{V}_w}{C_w}$

Setting $\mu_w' = \mu_w''$

$$\Delta \Pi = R T C_A$$

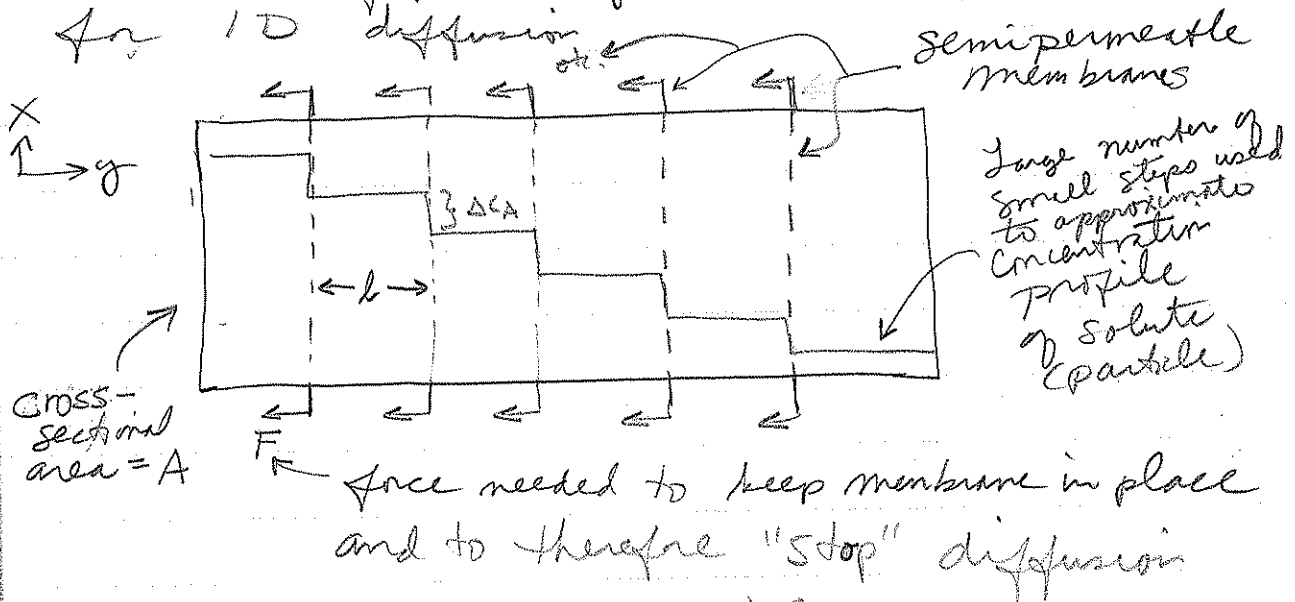
also

$$\Delta \Pi = R T (C_A' - C_A'') \text{ if } C_A'' \neq 0$$

universal gas constant

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



$$F = A \Delta T = A R T \Delta C_A$$

Force per unit volume of fluid:

$$\frac{F}{A l} = \frac{A R T \Delta C_A}{A l} = R T \frac{dC_A}{dy}$$

Force per mole

$$\mu_A = \mu_A^0 + R T \ln X_A$$

chemical potential

$$\frac{F}{A l} \cdot \frac{1}{C_A} = \frac{R T}{C_A} \frac{dC_A}{dy} = R T \frac{d \ln C_A}{dy}$$

When it is dilute,
 $\frac{d \ln C_A}{dy} \approx \frac{d \ln X_A}{dy}$ so

$$R T \frac{d \ln C_A}{dy} = - \frac{d}{dy} \mu_A^{\text{chem}} = - \vec{\nabla} \mu_A^{\text{chem}}$$

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:

- 6 -

Stokes Law:

$$v = \frac{F'}{6\pi\mu R_A}$$

← force on one molecule
← radius of molecule

$$F' = \frac{F}{N_{av}} = \frac{RT}{N_{av}} \frac{1}{C_A} \frac{dC_A}{dy}$$

$$v = \frac{RT}{6\pi\mu R_A N_{av} C_A} \frac{dC_A}{dy}$$

Since $C_A \cdot v = J_A = \text{flux of A} :$

$$J_A = \underbrace{\frac{RT}{6\pi\mu R_A N_{av}}}_{D_A} \frac{dC_A}{dy}$$

Note that R is known from $P=V-T$ experiments with "ideal" gases:

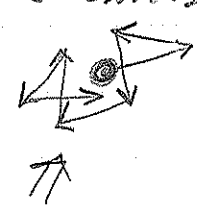
Combine "Charles" Law and "Boyles" law
 $PV = \text{const.} \cdot T$ (const. is different for different gases)

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

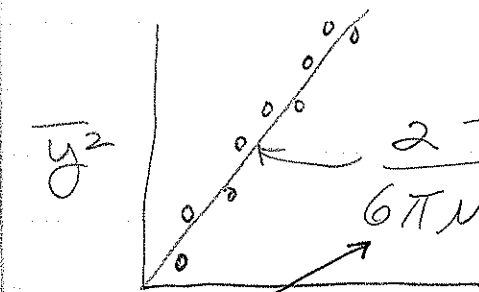
$$PV = nRT$$

← "universal" gas constant
← number of "moles"

In 1860, Stanislao Cannizzaro standardized the atomic weight scale by setting the molecular weight of O_2 at 16, so that 1 mole became defined as the number of molecules in 16 grams of O_2 . 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 O_2 , Brownian motion experiments can be used to determine N_{Av} .


 observe under a microscope

\Rightarrow keep track of the times the particle is at various locations to measure probability function $P(y)$, then determine $\overline{y^2} = \int_{-\infty}^{\infty} y^2 P(y) dy$



everything can be measured except N_{Av}

$\frac{2RT}{6\pi\eta R_A N_{Av}} = \text{slope}$

Experimentally, if a particle location is determined at the time increments Δt , then at any time t :

$$\overline{y^2(t)} = \sum_{i=1}^{t/\Delta t} y_i^2 / (t/\Delta t)$$

where y_i is the particle location at the i th time step.

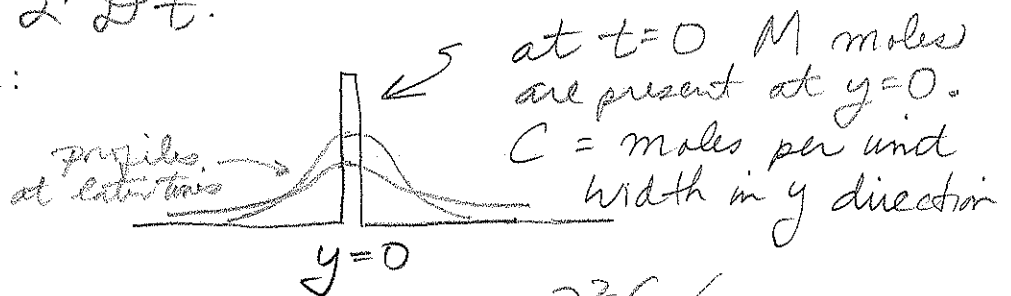
1926 Nobel Prize in Chemistry

Jean Perrin performed the experiment in 1906 and determined that $N_{Av} = 6.5 - 6.9 \times 10^{23}$. The size of molecules can also now be estimated. For liquid water 18 gram (1 mole) occupies 18 ml so $D \approx \sqrt[3]{0.018 \text{ L} \cdot \frac{1 \text{ m}^3}{1000 \text{ L}}} / N_{Av} = \frac{10^{-10} \text{ m}}{1 \text{ m}} = 3 \text{ \AA}$

In the early 1900's the existence of molecules was not accepted by all of 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 $\overline{y^2} = 2Dt$.

Example:



need to solve $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2}$

subject to $\int_{-\infty}^{\infty} C dy = M$

Solution is $C = \frac{M}{\sqrt{4\pi Dt}} \exp(-y^2/4Dt)$

calculate $\overline{y^2}$:

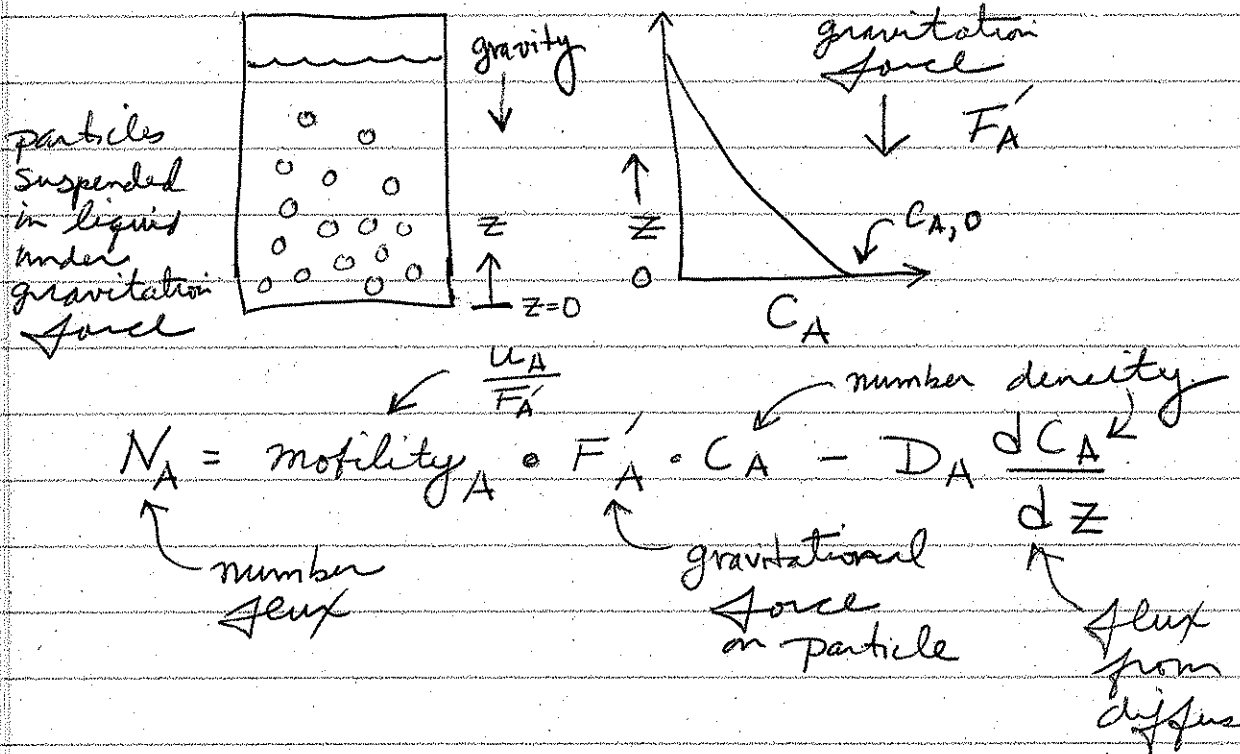
↑ Gaussian profile with $\sigma = (2Dt)^{1/2}$

$$\overline{y^2} = \frac{\int_{-\infty}^{\infty} y^2 C dy}{M}$$

$$= \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} y^2 \exp(-y^2/4Dt) dy$$

$$= 2Dt$$

Relation between Nernst-Einstein Equation and the Boltzmann Relation



at steady state, $N_A = 0$. also $F_A' = -m_A |g|$
 Substituting:

$$0 = \text{mobility}_A (-m_A) |g| C_A - D_A \frac{dC_A}{dz}$$

mass of particle corrected for buoyancy

so that

$$- \text{mobility}_A m_A |g| \frac{dz}{D_A} = \frac{dC_A}{C_A}$$

integrating from $z=0$ (where $C_A = C_{A,0}$) to z

$$- \text{mobility}_A m_A |g| \frac{z}{D_A} = \ln \frac{C_A}{C_{A,0}}$$

so that

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

But $m_A |g| z$ is the gravitation potential energy. So above relation is equivalent to Boltzmann relation if $\rightarrow D_A / \text{mobility}_A = kT$

Note that this expression is the Nernst-Einstein equation