# Kinetic Theory and molecular transport

Kinetic Theory is essentially a *statistical* theory of the motion of molecules. It can be used to *explain bulk properties of matter* since the sizes of molecules (or atoms) are *very* small compared to human-sized macroscopic objects like vials of liquid or bottles of gas. In other words, the number of molecules and interactions in most practical scenarios is a *huge* number. In Kinetic Theory, we consider *average* physical quantities such as speed, pressure, heat flux etc, since the huge number of molecules makes a mechanical calculation impractical. Inspired by the observation of **Brownian motion**, we shall assume molecular motion is a *random* process. This assumption of randomness will enable us to *calculate* average physical quantities based upon knowledge of their *probability distributions.*

Note a cubic metre of densely packed atoms will have about $1/\left(10^{-10}\right)^3 = 10^{30}$ atoms, since the size of an atom is about 10^{-10} m.

Indeed a mole of a chemical substance (e.g. about 18 grams of water) is defined to have **Avogadro's number** of molecules $\boxed{N_A = 6.02 \times 10^{23}}$
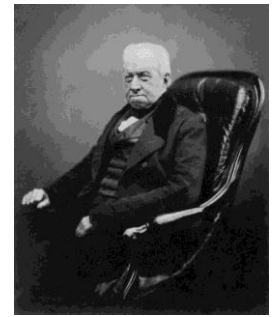
Robert Brown 1773-1858

Brownian motion – a random walk

Brownian motion, initially observed as the random jittering of pollen grains in a microscope slide, is due to the random jostling of molecular motion. In the base of the pollen grains, it is the smaller (invisible) air molecules which are colliding at random. How far will a given particle move in a specified time, given its motion is random? To analyse this in the simplest situation, let us consider motion in one direction in N steps of fixed length l. The caveat is that each step is either forward or backwards, and the direction is 'chosen' randomly.

The total displacement is $x = l \sum_{i=1}^{N} a_i$ where $a_i = -1 \text{ or } 1$

A sensible measure of the distance travelled is the *root-mean-square (RMS) displacement*

$$\sqrt{\langle x^2 \rangle} = l \sqrt{\left\langle \left(\sum_{i=1}^{N} a_i \right)^2 \right\rangle} = l \sqrt{\left\langle \sum_{i=1}^{N} a_i^2 + \sum_{i=1,i\neq j}^{N} \sum_{j=1}^{N} a_i a_j \right\rangle}$$

$$\left\langle \sum_{i=1}^{N} a_i^2 \right\rangle = N \quad \text{and} \quad \left\langle \sum_{i=1,i\neq j}^{N} \sum_{j=1}^{N} a_i a_j \right\rangle = 0 \longleftarrow \text{Since } a \text{ is a random choice between -1 and 1}$$

$$\therefore \boxed{\sqrt{\langle x^2 \rangle} = l\sqrt{N}}$$

We might use the RMS speed here $\sqrt{\langle v^2 \rangle}$

If the average molecular speed is $\langle v \rangle$, the number of steps in t seconds is $N = \dfrac{\langle v \rangle t}{l}$

Hence the random walk distance in t seconds is predicted to be:

$$\boxed{\sqrt{\langle x^2 \rangle} = l\sqrt{N} = \sqrt{l \langle v \rangle t}}$$

The step size l can be associated with the **mean free path** between molecular collisions. We can define the mean free path to be the average distance travelled by a molecule in time t divided by by the number of molecules it will likely collide with in that time.

Random walk. Max step size = 1, N = 10000
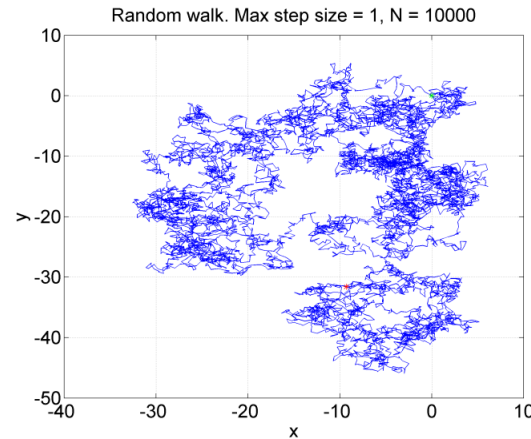
Note in this MATLAB simulation both the angle of movement and the step length are both uniformly distributed. The angle between 0 and 360°, and the step from zero to the maximum of unity.

Amedeo Avogadro 1776-1856

$$l = \frac{\sqrt{\langle v^2 \rangle} t}{\underbrace{\pi d^2 \sqrt{2}}_{\text{'Interaction volume'}} \sqrt{\langle v^2 \rangle} t \times \underbrace{n}_{\substack{\text{number of} \\ \text{molecules} \\ \text{per unit} \\ \text{volume}}}}$$

Distance travelled by molecule

$$\boxed{l = \frac{1}{\pi \sqrt{2} d^2 n}}$$

Mean free path

The interaction volume is root 2 larger because all molecules are in *relative* motion. Hence the length of the 'interaction tube' is proportional to the average *relative* speed

velocities of molecules i and j

$$\langle v_{rel} \rangle = \sqrt{\left\langle \left| \mathbf{v}_i - \mathbf{v}_j \right|^2 \right\rangle}$$

$$\langle v_{rel} \rangle = \sqrt{\left\langle \left(v_i^2 + v_j^2 - 2\mathbf{v}_i \cdot \mathbf{v}_j \right) \right\rangle}$$

$$\langle v_{rel} \rangle = \sqrt{2 \langle v^2 \rangle - 2 \langle \mathbf{v}_i \cdot \mathbf{v}_j \rangle}$$

$$\langle v_{rel} \rangle = \sqrt{2} \sqrt{\langle v^2 \rangle}$$

d

$\sqrt{2}\sqrt{\langle v^2 \rangle} t$

Colliding particles, assumed to be circular with diameter d

Notes inspired by *The Feynmann Lectures on Physics* (vol 1 43-3), http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/menfre.html#c1 and the Sixth Form Physics course taught at Winchester College by Dr John Cullerne

We can determine the **mean free path** for an ideal gas by using the **Ideal Gas Equation**

Since the number of moles is $\dfrac{nV}{N_A}$ ← volume

pressure → $pV = \dfrac{nV}{N_A}RT$ ← Absolute temperature

Molar gas constant
$R = 8.314\,\mathrm{Jmol^{-1}K^{-1}}$

$\therefore n = \dfrac{p}{k_B T}$

Boltzmann's constant $k_B = 1.38 \times 10^{-23}\,\mathrm{JK^{-1}}$

Hence $\boxed{l = \dfrac{k_B T}{\pi\sqrt{2}d^2 p}}$

If we divide this by the particle diameter d we arrive at **Knudsen's number (Kn)**. This dimensionless constant determines whether our statistical mechanics argument is valid, or whether a 'continuum' concept is needed.

The latter model is what is used to describe much of **fluid mechanics** i.e. where we consider the fluid as a continuously varying entity rather than a series of discrete, and randomly moving, molecules colliding.

$\boxed{\begin{array}{ll} \mathrm{Kn} \ll 1 & \text{Continuum} \\ \mathrm{Kn} > 1 & \text{Statistical mechanics} \end{array}}$

For a typical air molecule on Earth
$d = 0.3\mathrm{nm},\ p = 10^5\,\mathrm{Pa},\ T = 293K$
$\therefore l = 1.0 \times 10^{-7}\,\mathrm{m}$

$\therefore \mathrm{Kn} = \dfrac{l}{d} = \boxed{333}$

So a statistical argument is justified

Mean free path and the Beer-Lambert Law
An alternative interpretation of the mean free path is to consider the attenuation of a molecular beam which passes through a volume randomly filled with n absorbing molecules per unit volume.

Molecule with cross sectional 'colliding area' $\sigma = \pi d^2$

I Beam intensity (molecules per unit area per second)
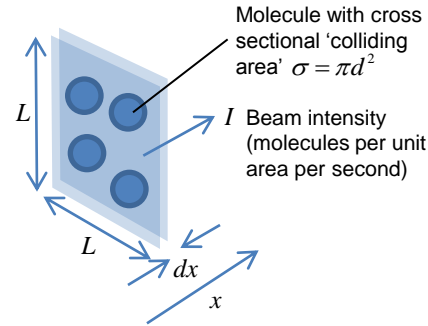
The change in intensity over length dx is

$dI = -I \times \text{probability of absorbtion between } x \text{ and } x + dx$

$dI = -I \times \dfrac{\text{molecules in } L^2 dx \times \text{molecule area}}{L^2}$

$dI = -I \times \dfrac{nL^2 dx \times \sigma}{L^2}$

$dI = -In\sigma dx$

$\therefore \int_{I_0}^{l} \dfrac{dI}{I} = -n\sigma x$

$\ln \dfrac{I}{I_0} = -n\sigma x$
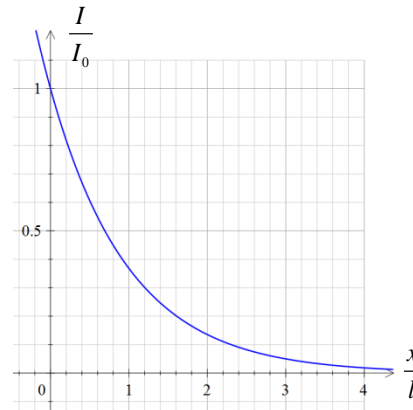
$\boxed{I = I_0 e^{-n\sigma x}}$

This **exponential** decrease of beam intensity implies the probability $p(x)$ of a beam 'surviving 'absorption between x and $x +$ dx metres must be proportional to
$e^{-n\sigma x}$

$p(x) = ke^{-n\sigma x} \qquad \int_0^\infty p(x)dx = 1$

$k\int_0^\infty e^{-n\sigma x}dx = 1 \Rightarrow k\left[-\tfrac{1}{n\sigma}e^{-n\sigma x}\right]_0^\infty = 1$

$\therefore k = n\sigma \quad \therefore \boxed{p(x) = n\sigma e^{-n\sigma x}}$

The mean free path l can be thought of as the mean distance before a absorption:

$l = E[x] = \int_0^\infty x p(x) dx = \int_0^\infty x n\sigma e^{-n\sigma x}dx$

$l = \left[-x n\sigma \tfrac{1}{n\sigma}e^{-n\sigma x}\right]_0^\infty - \int_0^\infty -\tfrac{1}{n\sigma}e^{-n\sigma x}n\sigma dx$

$l = 0 + \left[-\tfrac{1}{n\sigma}e^{-n\sigma x}\right]_0^\infty$

$\boxed{l = \dfrac{1}{n\sigma}}$

This is very similar to the result derived on the previous page

$\boxed{l = \dfrac{1}{\pi\sqrt{2}d^2 n}}$ if $\sigma = \pi d^2$

If we consider a beam moving through stationary molecules then we can omit the square root of two factor as we don't need to consider relative velocity.

In summary: $\boxed{I = I_0 e^{-x/l}}$ Attenuation of a molecular beam passing through a molecular medium, where l is the mean free path

The survival *probability density function* is $\boxed{p(x) = \dfrac{e^{-x/l}}{l}}$

Diffusion and Fick's Law
A molecular *concentration gradient* can drive diffusion of molecules. This is particularly important across cell membranes in biology. The molecular flux of diffusing molecules J (molecules per second per unit cross sectional area) is, in the x direction:

'one second of molecules', per unit area cross section, in the x direction →

$J_x = \tfrac{1}{6}\sqrt{\langle v^2 \rangle} \times \left(-\dfrac{dn}{dx} \times l\right)$ ← change in molecules per unit volume between collisions

This allows the **diffusion constant** in the usual expression of Fick's Law to be expressed in terms of RMS molecular velocity and mean free path

$\boxed{\begin{array}{l} J_x = -D\dfrac{dn}{dx} \\ \therefore D = \tfrac{1}{3}l\sqrt{\langle v^2 \rangle} \end{array}}$ i.e. **molecular flux is proportional to concentration gradient**

Fick's Law can also be applied to the transport of *heat* based on a *temperature gradient* (**Fourier's Law** of **conduction**) and transport of *momentum* in a fluid with a *velocity gradient* (we call this **viscosity**)

Molecular flux
$$J_x = -\tfrac{1}{3}l\sqrt{\langle v^2 \rangle}\frac{dn}{dx}$$

$$J_x = -D\frac{dn}{dx}$$
$$D = \tfrac{1}{3}l\sqrt{\langle v^2 \rangle}$$

Fick's Law: Molecular flux is proportional to concentration gradient

Viscosity
$$\frac{f_x}{A} = \tfrac{1}{3}l\sqrt{\langle v^2 \rangle}\rho\frac{dv_x}{dz}$$

Molecular flux is now rate of change of momentum per unit area i.e. force per unit area.

n becomes momentum per unit volume ρv_x

Note in this case viscosity results from a velocity gradient *perpendicular* to the fluid flow

Newtonian stress-strain rate equation in fluid flow
$$\frac{f_x}{A} = \eta\frac{dv_x}{dz}$$

i.e. stress (fore per unit area) is proportional to the *shear velocity* The constant of proportionality is the *viscosity*

$$\eta = \tfrac{1}{3}l\sqrt{\langle v^2 \rangle}\rho$$

Heat flux
$$\dot{Q}_x = -\tfrac{1}{3}l\sqrt{\langle v^2 \rangle}\rho c_V \frac{dT}{dx}$$

Molecular flux is now heat flux. c_V is the *specific* heat capacity and T the temperature.

n becomes heat per unit volume $\rho c_V T$

Fourier's law of conduction
$$\dot{Q}_x = -k\frac{dT}{dx}$$
$$k = \tfrac{1}{3}l\sqrt{\langle v^2 \rangle}\rho c_V$$

i.e. **heat flux is proportional to temperature gradient**

Particle flux in a 'Boltzmann gas' is the number of collisions expected per unit area upon a surface in contact with the gas.

Assume a gas has n particles per unit volume.

Consider a surface centred at the origin of the x,y plane, whole normal is the z axis. The number of particles that impact the surface (of unit area) in one second (i.e. the particle flux) is:

$$\Phi = \int_{\theta=0}^{\frac{1}{2}\pi}\int_{\phi=0}^{2\pi}\int_{v=0}^{\infty} n\times\underbrace{\frac{\sin\theta\, d\theta\, d\phi}{4\pi}}_{\text{I}}\times\underbrace{v\cos\theta}_{\text{II}}\times\underbrace{p(v)dv}_{\text{III}}$$

I Fraction of particles that are arriving from polar angle θ from the z axis and ϕ anticlockwise from the x axis. This is the ratio of an area element of a unit sphere divided by the area of the unit sphere. This is essentially a 'solid angle'

II Projection of (incoming) velocity in the z direction. Note we don't include outgoing particles, hence the range of θ is 0 to $\pi/2$ radians, not π.

III Number of particles with velocity between v and $v + dv$
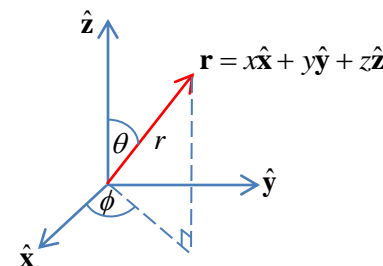
$$\Phi = \tfrac{1}{4\pi}n\int_{\theta=0}^{\frac{1}{2}\pi}\sin\theta\cos\theta\, d\theta\int_{\phi=0}^{2\pi}d\phi\int_{v=0}^{\infty}vp(v)dv$$

$$\Phi = \tfrac{1}{4\pi}n\int_{\theta=0}^{\frac{1}{2}\pi}\tfrac{1}{2}\sin 2\theta\, d\theta\times 2\pi\int_{v=0}^{\infty}vp(v)dv$$

$$\Phi = \tfrac{1}{4}n\left[-\tfrac{1}{2}\cos 2\theta\right]_0^{\frac{1}{2}\pi}\times\int_{v=0}^{\infty}vp(v)dv$$

$$\Phi = \tfrac{1}{4}n\left\{\left(-\tfrac{1}{2}(-1)\right)-\left(-\tfrac{1}{2}(1)\right)\right\}\times\bar{v}$$

$$\therefore \Phi = \tfrac{1}{4}n\bar{v}$$

$$\mathbf{r} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

Conversion between Cartesian and polar coordinates
$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

Pressure from kinetic theory – a simplified derivation that gives the correct more general result!

Assume particles collide *elastically* with the walls of a container.
Since in an elastic collision the speed of wall approach = speed of recession the impulse exerted on the walls in each x,y,z direction per collision is:

$$\Delta p_{x,y,z} = 2mv_{x,y,z}$$

If we assume particles are contained within a cube of side a, the time between collisions with a given wall is:

$$\Delta t_{x,y,z} = \frac{2a}{v_{x,y,z}}$$
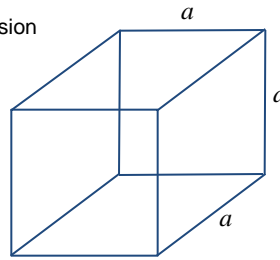
The factor of two is there because in any or the x,y,z directions, a particle must collide with the opposite wall before rebounding to make a second collision with a given wall.

The total average force exerted on a given wall of area a^2 is the average rate of change of momentum times the number of particles N in the cube

$$f_{x,y,z} = \frac{\Delta p_{x,y,z}}{\Delta t_{x,y,z}} = \frac{2mv_{x,y,z}}{2a/v_{x,y,z}} = \frac{mv_{x,y,z}^2}{a} \quad \text{force due to one collision}$$

$$\therefore \overline{F_{x,y,z}} = \frac{Nm\overline{v_{x,y,z}^2}}{a} \quad \text{Total } \textit{average} \text{ force on one wall}$$

Define the particle density $\quad \rho = \frac{Nm}{a^3} \quad \therefore \frac{Nm}{a} = \rho a^2 \quad \therefore \overline{F_{x,y,z}} = \rho a^2 \overline{v_{x,y,z}^2}$

Now particle speed is given by $\quad v^2 = v_x^2 + v_x^2 + v_x^2$

Hence since all velocities are deemed to be random, the mean squared speed is

$$\overline{v^2} = 3\overline{v_{x,y,z}^2}$$

Therefore average *pressure* on each wall is: $\quad P = \frac{\overline{F_{x,y,z}}}{a^2}$

Hence: $\quad \boxed{P = \frac{1}{3}\rho\overline{v^2}}$

Pressure from kinetic theory – using Boltzmann statistics

$$P = \int_{\theta=0}^{\frac{1}{2}\pi} \int_{\phi=0}^{2\pi} \int_{v=0}^{\infty} \underbrace{n \times \frac{\sin\theta d\theta d\phi}{4\pi}}_{\text{I}} \times \underbrace{v\cos\theta}_{\text{II}} \times \underbrace{mv\cos\theta}_{\text{III}} \times \underbrace{p(v)dv}_{\text{IV}}$$

I   Fraction of particles that are arriving from polar angle θ from the z axis and ϕ anticlockwise from the x axis. This is the ratio of an area element of a unit sphere divided by the area of the unit sphere. This is essentially a 'solid angle'

II Projection of (incoming) velocity in the z direction. Note we don't include outgoing particles, hence the range of θ is 0 to $\pi/2$ radians, not π.

III Projection of impulse applied to the x,y plane unit surface in the z direction . Purely elastic collisions are assumed .

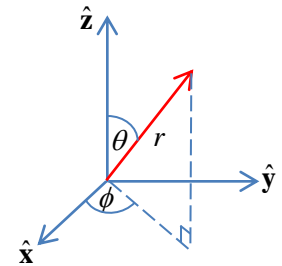IV Number of particles with velocity between v and $v + \mathrm{d}v$

$$P = \frac{1}{2\pi}nm \int_{\theta=0}^{\frac{1}{2}\pi} \sin\theta\cos^2\theta d\theta \int_{\phi=0}^{2\pi} d\phi \int_{v=0}^{\infty} v^2 p(v)dv$$

$$P = \rho\overline{v^2} \int_{\theta=0}^{\frac{1}{2}\pi} \sin\theta\cos^2\theta d\theta$$

$$\frac{d}{d\theta}\cos^3\theta = -3\cos^2\theta\sin\theta$$

$$\therefore \int_{\theta=0}^{\frac{1}{2}\pi} \sin\theta\cos^2\theta d\theta = \left[-\frac{1}{3}\cos^3\theta\right]_0^{\frac{1}{2}\pi} = (0) - \left(-\frac{1}{3}\right) = \frac{1}{3}$$

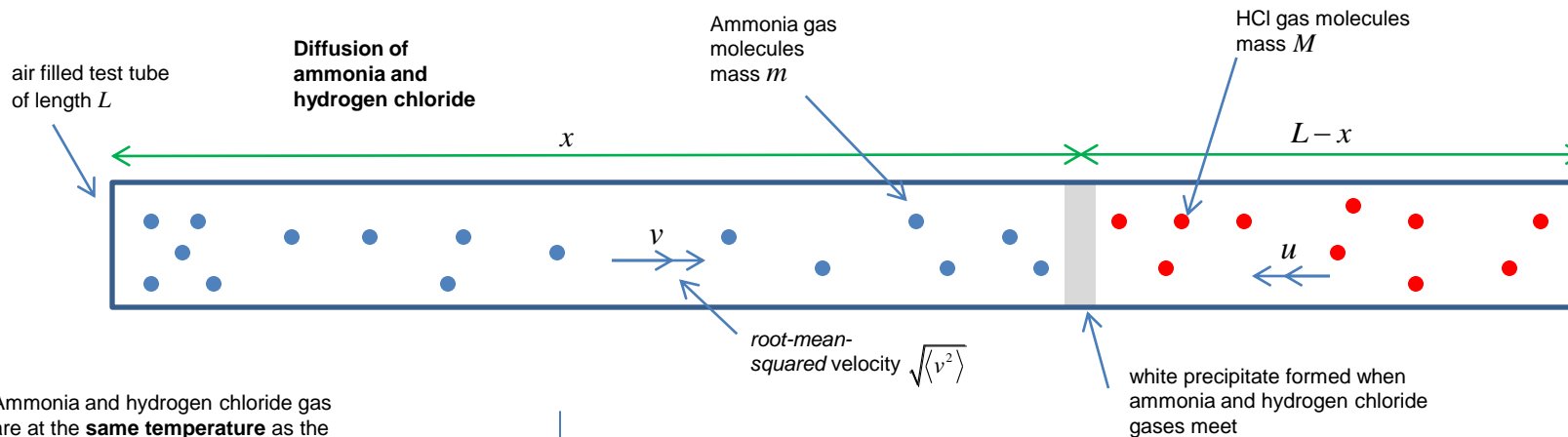$$\boxed{\therefore P = \frac{1}{3}\rho\overline{v^2}}$$

Ludwig Boltzmann
1844-1906

Graham's law of molecular diffusion

Kinetic theory shows us the diffusion distance of molecules in thermal *equilibrium varies inversely to the square root of their molecular weight.*

To explain, consider an air filled tube with Ammonia gas introduced at one and, and Hydrogen Chloride gas introduced at the other.

Ammonia gas molecules mass m

HCl gas molecules mass M

Diffusion of ammonia and hydrogen chloride

air filled test tube of length L

x

$L-x$

v

u

root-mean-squared velocity $\sqrt{\langle v^2 \rangle}$

white precipitate formed when ammonia and hydrogen chloride gases meet

Thomas Graham
1805-1869

Ammonia and hydrogen chloride gas are at the **same temperature** as the air molecules in the tube. **This means their average kinetic energy is the same**

$$\tfrac{1}{2}mv^2 = \tfrac{1}{2}Mu^2$$

$$\therefore \frac{v}{u} = \sqrt{\frac{M}{m}}$$

The precipitate is formed after t seconds at a distance x from the ammonia end of the tube

$$v = \frac{x}{t}, \quad u = \frac{L-x}{t}$$

$$\therefore \frac{x}{L-x} = \frac{v}{u}$$

$$\therefore \boxed{\frac{x}{L-x} = \sqrt{\frac{M}{m}}}$$

So diffusion distance $x \propto \dfrac{1}{\sqrt{m}}$

Molecular masses
NH$_3$ 17
HCl   36.5

Therefore expect:

$$\frac{x}{L-x} = \sqrt{\frac{36.5}{17}} \approx \boxed{1.47}$$

i.e. about 3:2