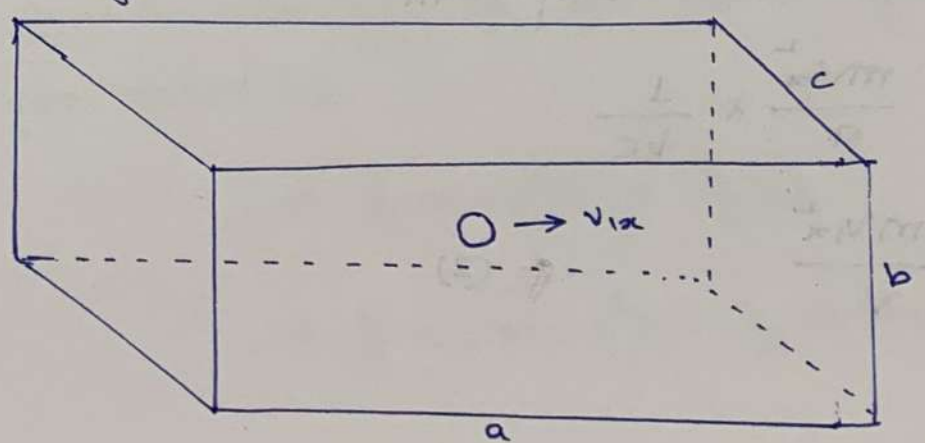
Kinetic theory of gases

We saw earlier that the solution for the average pressure of a gas molecule by considering non-interacting particles partition function in a box naturally yielded the ideal gas equation. Hence, a gas may not be considered as a continuum but a collection of discrete particles in constant motion. The model considering constant motion of discrete particles colloiding with each other and with the walls of the container gives rise to the kinetic theory of gases.

Consider a single partide in a box undergoing translation. The pressure that it exerts on the walls of the box is due to its collision with the walls. At any instant of time, the velocity v_1 has three components v_{1x}, v_{1y} and v_{1z} along the three coordinate axes. Let us first consider the motion along the x-axis.



The x-component of the momentum $= mv_{ix}$ of the particle

When the collision with the wall is perfectly elastic, the motion of the particle is reversed.

$\Rightarrow$ The x-component of the momentum $= -mv_x$ of the particle after collision with the wall

$\Rightarrow$ Change in momentum $= mv_{ix} - (-mv_{ix})$

$$\Delta p_{ix} = 2mv_{ix}$$

When the particle has reached its original position after traversing a distance of $2a$, the time elapsed $\Delta t = 2a/v_{ix}$

Following the definition of force, the force exerted by the particle on right wall

$$F_1 = \frac{\Delta P_{ix}}{\Delta t}$$

$$\Rightarrow F_{ix} = \frac{2mv_{ix} \cdot v_{ix}}{2a}$$

$$\Rightarrow F_{ix} = \frac{mv_{ix}^2}{a} \quad -(1)$$

The pressure exerted on the wall

$$P_1 = \frac{mv_{ix}^2}{a} \times \frac{1}{bc}$$

$$\Rightarrow P_1 = \frac{mv_{ix}^2}{V} \quad -(2)$$

For an N-particle system, the total pressure exerted by all the particles will be

$$P = \frac{m}{V} \sum_{i=1}^{N} v_{ix}^2 \qquad - (3)$$

The average value of the square of velocity is obtained as

$$\langle v_x^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} v_{ix}^2$$

$$\Rightarrow PV = mN \langle v_x^2 \rangle \qquad - (4)$$

Since we do not observe any motion of the box on collision of the molecules with the walls,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

Since velocity is a vector,

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$\Rightarrow \langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

$$\Rightarrow PV = \frac{1}{3} N m \langle v^2 \rangle \qquad - (5)$$

It was shown earlier that the average translational energy of an ideal gas equals $\frac{3}{2} k_B T$ per molecule

$$\Rightarrow \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

$$\Rightarrow \frac{1}{2} N_A m \langle v^2 \rangle = \frac{3}{2} k_B N_A T$$

$$\Rightarrow \frac{1}{3} M \langle v^2 \rangle = RT \qquad -(6)$$

where M is the molar mass of the gas.

$$\Rightarrow \langle v^2 \rangle = \frac{3RT}{M}$$

$$\Rightarrow \langle v^2 \rangle^{1/2} = \sqrt{\frac{3RT}{M}} \qquad -(7)$$

The quantity $\langle v^2 \rangle^{1/2}$ is called the root mean square velocity.

$$v_{rms} = \sqrt{\frac{3RT}{M}} \qquad -(8)$$

As can be seen that the RMS value of the speed is only a mean value. One may not expect every single molecule to have this exact value of speed. In other words, since there are a lot of molecules, different molecules may have different speeds resulting in the RMS speed given by Eqn (8). Therefore, it is desirable to determine the distribution of speeds.

Let $h(v_x, v_y, v_z)\,dv_x dv_y dv_z$ be the fraction of molecules that have velocity components between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and v_z and $v_z + dv_z$. It is assumed that the probability the x-component has a particular value is independent of the y and z components i.e. the probability distributions are independent in each direction. Following this, we can write

$$h(v_x, v_y, v_z) = f(v_x) f(v_y) f(v_z) \quad - (9)$$

where $f(v_i)$ are the probability distributions of the individual components. Further, all these distributions must be identical. These distributions are functions of speeds only.

$$\ln h(\mathbf{v}) = \ln f(v_x) + \ln f(v_y) + \ln f(v_z)$$

$$\Rightarrow \frac{\partial}{\partial v_x} (\ln h(v))_{v_y, v_z} = \frac{d}{dv_x} (\ln f(v_x))$$

$$\frac{\partial}{\partial v_x} (\ln h(v))_{v_y, v_z} = \frac{d \ln h}{dv} \left(\frac{\partial v}{\partial v_x}\right)_{v_y, v_z} = \left(\frac{v_x}{v}\right) \frac{d \ln h}{dv}$$

$$\Rightarrow \frac{v_x}{v} \frac{d \ln h}{dv} = \frac{d}{dv_x} (\ln f(v_x))$$

$$\Rightarrow \frac{d \ln h(v)}{v\, dv} = \frac{d \ln f(v_x)}{v_x\, dv_x} = \frac{d \ln f(v_y)}{v_y\, dv_y} = \frac{d \ln f(v_z)}{v_z\, dv_z} \quad - (10)$$

Since v_x, v_y and v_z are independent of one another, each term in Eq^n (10) must be equal to a constant.

$$\frac{d \ln f(v_i)}{v_i\, dv_i} = -\gamma$$

$$\Rightarrow f(v_i) = A e^{-\gamma v_i^2} \quad - (11)$$

A and γ need to be determined since $f(v_i)$ is a probability distribution,

$$\int_{-\infty}^{\infty} f(v_x)\, dv_x = 1$$

$$\Rightarrow \int_{-\infty}^{\infty} A e^{-\gamma v_x^2}\, dv_x = 1$$

$$A\int_{-\infty}^{\infty} e^{-\gamma v_x^2}\, dv_x = 2A\int_{0}^{\infty} e^{-\gamma v_x^2}\, dv_x = 1$$

$$\Rightarrow 2A\left(\frac{\pi}{4\gamma}\right)^{1/2} = 1$$

$$\Rightarrow A = \sqrt{\frac{\gamma}{\pi}}$$

$$\Rightarrow f(v_x) = \sqrt{\frac{\gamma}{\pi}}\, e^{-\gamma v_x^2} \qquad -(12)$$

γ can be evaluated using Eq^n (7)

$$\langle v_x^2 \rangle = \frac{RT}{M}$$

$$\Rightarrow \int_{-\infty}^{\infty} v_x^2 f(v_x)\, dv_x = \frac{RT}{M}$$

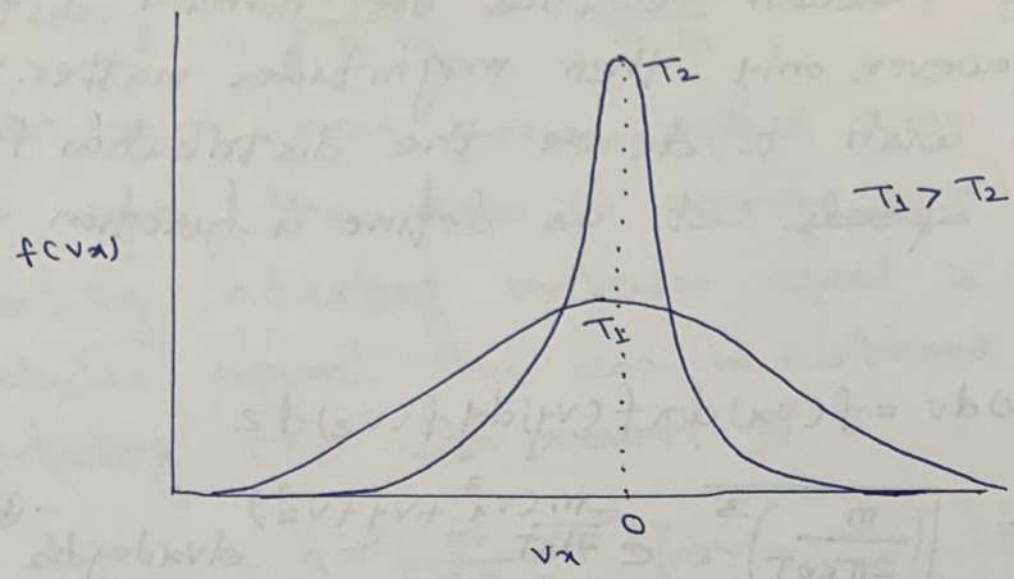
$$\Rightarrow 2\sqrt{\frac{\gamma}{\pi}}\int_{0}^{\infty} v_x^2 e^{-\gamma v_x^2}\, dv_x = \frac{RT}{M}$$

$$\Rightarrow \left(2\sqrt{\frac{\gamma}{\pi}}\right)\left(\frac{1}{4\gamma}\sqrt{\frac{\pi}{\gamma}}\right) = \frac{RT}{M}$$

$$\Rightarrow \gamma = \frac{M}{2RT}$$

$$\Rightarrow f(v_x) = \sqrt{\frac{M}{2\pi RT}}\, e^{-\frac{Mv_x^2}{2RT}} \qquad -(13)$$

Eq^n (13) is the equation of a Gaussian distribution. It is to be noted that the distribution is a function of temperature. Typical distributions look like the ones shown.



The mean velocity is zero and the molecules can travel in positive or negative directions. The average value of v_x can be determined as

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x)\, dv_x$$

$$= \sqrt{\frac{M}{2\pi RT}} \int_{-\infty}^{\infty} v_x e^{-\frac{Mv_x^2}{2RT}}\, dv_x$$

$$= 0$$

This distribution is called Maxwell distribution of velocities. It is a Gaussian distribution indicating that the molecules on an average are moving in positive and negative directions equally. The net result is zero average velocity along a particular direction, a conclusion which is also intuitive.

Maxwell - Boltzmann distribution :

The molecular velocities are normally distributed. However, only their magnitudes matter. So we now wish to derive the distribution for molecular speeds. Let us define a function as follows :

$$F(v)\,dv = f(v_x)\,dx\, f(v_y)\,dy\, f(v_z)\,dz$$

$$\Rightarrow F(v)\,dv = \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}\; e^{\frac{-m(v_x^2+v_y^2+v_z^2)}{2k_BT}}\, dv_x dv_y dv_z \quad -(14)$$

Consider the rectangular coordinate system in which the distances along the axes are v_x, v_y and v_z. This space is called the velocity space. Since the gas is isotropic, we define a spherical shell $4\pi v^2 dv$ in which the speed range is v and $v+dv$.

$$\Rightarrow F(v)\,dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\frac{-mv^2}{2k_BT}}\, 4\pi v^2\, dv \quad -(15)$$

Eq^n (15) gives the probability distribution of a molecule having a speed between v and $v+dv$.

Therefore,

$$\langle v \rangle = \int_0^\infty v\, F(v)\, dv$$

$$= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2k_BT}\, dv$$

On integration,

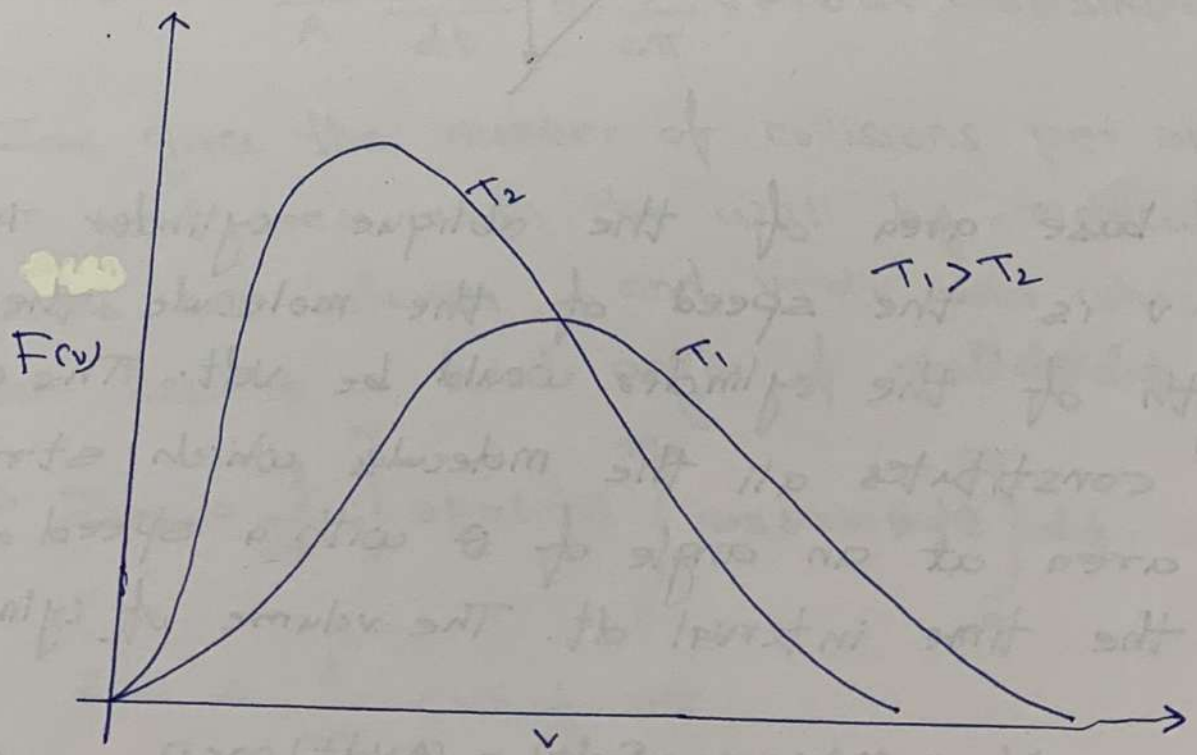
$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \qquad -(16)$$

Unlike root mean square speed given by Eq^n (8), $\langle v \rangle$ gives the mean or average speed. Another quantity indicating molecular speed is the most probable speed. This can be obtained by differentiating $F(v)$ with respect to v.

$$\frac{d}{dv}F(v) = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\left(2v - \frac{mv^3}{k_BT}\right)e^{\frac{-mv^2}{2k_BT}} = 0$$

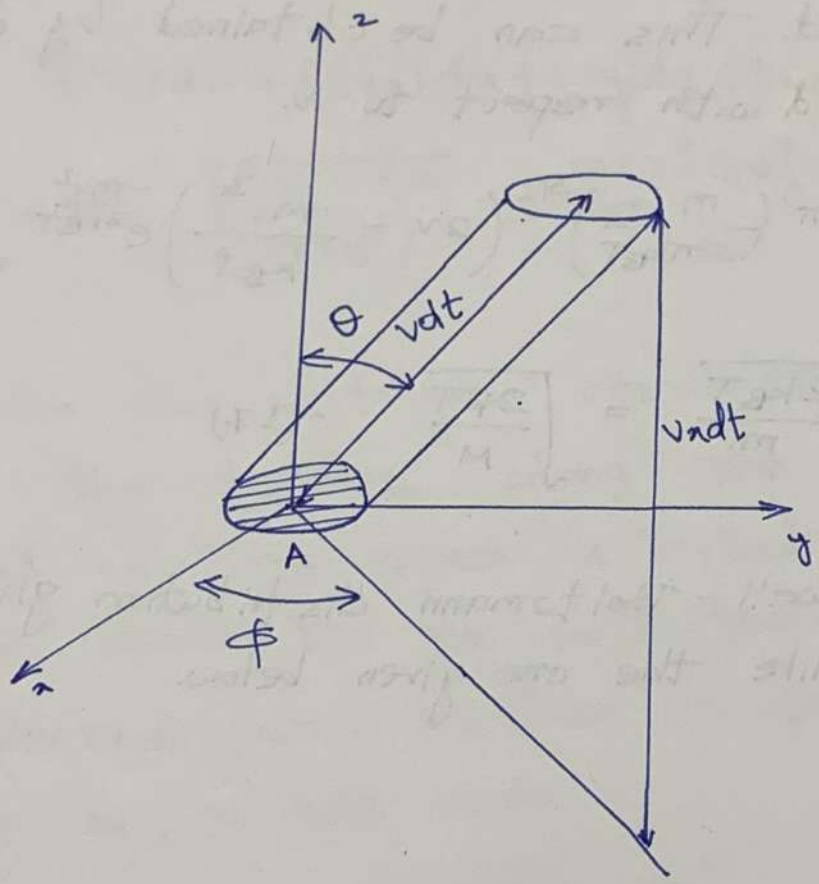
$$\Rightarrow v_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}} \qquad -(17)$$

A typical Maxwell-Boltzmann distribution given by Eq^n (15) looks like the one given below.



Collision frequency :

We now wish to derive an expression for the frequency with which the gas molecules colloid with the container walls. Consider the following figure.



The base area of the oblique cylinder is A. If v is the speed of the molecule then the length of the cylinder would be vdt. The cylinder constitutes all the molecules which strike the area at an angle of θ with a speed of v in the time interval dt. The volume of cylinder

$$V = (A)(v\cos\theta dt) = (Avdt)\cos\theta \qquad -(18)$$

If ρ is the average density of the gas then the number of molecules in the volume

$$N = \rho (A v dt) \cos\theta \qquad -(19)$$

It is to be noted that ρ is the number density; $\rho = N/V$.

Fraction of molecules with speeds in a range of v and $v+dv = F(v)\,dv$

Fraction of molecules traveling within a solid angle of range θ and $\theta + d\theta$ and ϕ and $\phi + d\phi$

$$= \sin\theta\, d\theta\, d\phi / 4\pi$$

$\Rightarrow$ Number of molecules colloiding with area A from a specified direction in time interval dt

$$dN_{coll} = \rho (A v dt) \cos\theta\; F(v)\,dv\; \frac{\sin\theta\, d\theta\, d\phi}{4\pi}$$

$$\Rightarrow dZ_{coll} = \frac{1}{A}\frac{dN_{coll}}{dt} = \frac{\rho}{4\pi} v F(v)\,dv \cos\theta \sin\theta\, d\theta\, d\phi$$

dZ_{coll} gives the number of collisions per unit time per unit area with the wall by molecules whose speeds are between v and $v+dv$ and whose direction lies in a solid angle of $\sin\theta\, d\theta\, d\phi$.

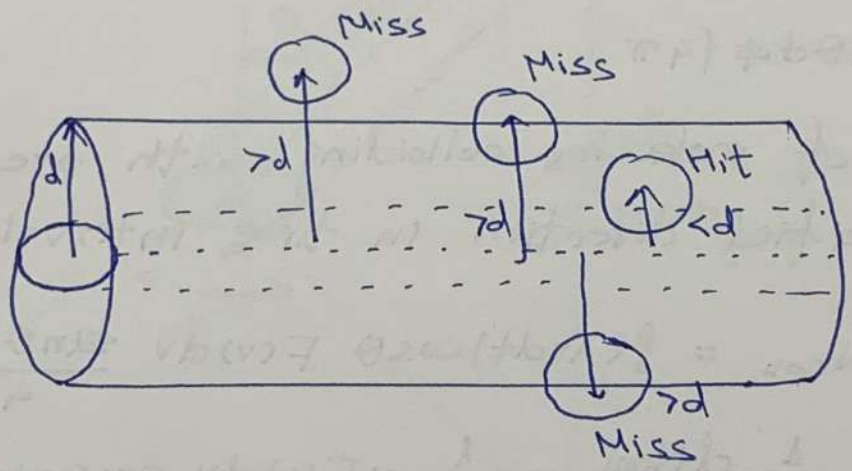
$$\Rightarrow Z_{coll} = \frac{\rho}{4\pi} \int_0^\infty v F_v(dv) \int_0^{\pi/2} \cos\theta \sin\theta\, d\theta \int_0^{2\pi} d\phi \qquad -(20)$$

$$\Rightarrow Z_{coll} = \frac{\rho}{4\pi} \langle v \rangle \frac{1}{2} 2\pi$$

$$\Rightarrow Z_{coll} = \frac{\rho}{4} \langle v \rangle \qquad -(21)$$

Mean free path:

Let us consider a gas consisting of hard spheres of diameter d. We take a test sphere which moves through stationary spheres and undergoes collision. While doing so, it sweeps a cylinder of cross-section $\frac{\pi d^2}{4}$. However, the effective cross-section of the collision cylinder will be πd^2 due to the situation shown in the figure given below.



The collision cross-section area is denoted by σ. Hence collision volume $= \sigma \langle v \rangle dt$. If f is the number density then

$$dN_{coll} = f\sigma \langle v \rangle dt \quad - (22)$$

$$\Rightarrow Z_A = \frac{dN_A}{dt} = f\sigma \sqrt{\frac{8k_BT}{\pi m}} \quad - (23)$$

The above equation is true for a moving sphere in a collection of static spheres. The correction for motion of other spheres

can be made by using reduced mass μ.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\Rightarrow \mu = \frac{m}{2}$$

The average velocity must be corrected to average relative velocity (speed)

$$\langle v_r \rangle = \sqrt{2} \langle v \rangle$$

The above two conditions give the correct expression for collision frequency as

$$Z_A = \sqrt{2} f \sigma \langle v \rangle \qquad - (24)$$

with $\langle v \rangle$ being calculated by reduced mass.

If a molecule travels at an average speed of $\langle v \rangle$ and makes Z_A collisions per unit time then the average distance travelled by the molecule between two collisions will be

$$l = \frac{\langle v \rangle}{Z_A}$$

$$\Rightarrow l = \frac{\langle v \rangle}{\sqrt{2} f \sigma \langle v \rangle}$$

$$\Rightarrow l = \frac{1}{\sqrt{2} f \sigma} \qquad - (25)$$

For an ideal gas, $f = PN_A / RT$

$$\Rightarrow l = \frac{RT}{\sqrt{2} N_A P \sigma} \qquad - (26)$$

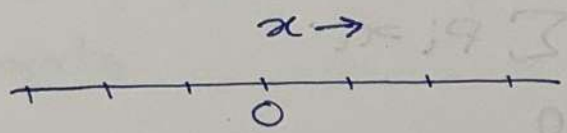
It can be seen from Eq^{n} (26) that the mean free path is directly proportional to temperature and inversely proportional to the pressure of the ideal gas. When $l >> \sigma$, the ideality in the gas can be expected.

Diffusion and random walks

As seen from the kinetic theory of gases, the molecules of a gas are in continuous motion and undergo collisions with the walls and with one another. These molecular motions give rise to the phenomenon of diffusion which can be modelled as random walks.

1-D random walk:

Imagine a particle confined to move along a line. The line is discretized as shown below.



At time $t = 0$, the particle starts at $x = 0$. Since the particle is "walking" "randomly", and is confied to be at one of the discrete points only, at at point, it can either move along the $+x$ axis or along the $-x$ axis one step. After reaching the new position, the particle again gets to make a random choice.

All the steps are assumed to be of equal interval 'l' and there is an equal probability of the walker to move in either directions. If the displacement at each step is denoted by s_i then

$$s_i = \begin{cases} +l & \text{with probability } 1/2 \\ -l & \text{with probability } 1/2 \end{cases}$$

After N steps the position (displacement) of the particle will be

$$x(N) = \sum_{i=1}^{N} s_i \qquad -(1)$$

The average distance that the particle moves

$$\langle x \rangle = \sum P_i x_i$$

$$= 0$$

This means that the average position of the particle is at the origin. But this does not mean that the particle does not move at all. We get a probability distribution. Hence, the spread of the distribution will give an idea of the extent with which the particle has moved. This can be obtained as follows.

$$x^2(N) = \left(\sum_{i=1}^{N} s_i\right)^2$$

$$= \sum_{i=1}^{N} s_i \sum_{j=1}^{N} s_j$$

$$= \sum_{i=1}^{N} s_i^2 + \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} s_i s_j$$

Now consider the quantity $s_i s_j$, $j \neq i$.

$$s_i s_j = \begin{cases} l^2 & \text{with probability of } 1/2 \\ -l^2 & \text{with probability of } 1/2 \end{cases}$$

$$\Rightarrow \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} s_i s_j = 0$$

$$\Rightarrow x^2(N) = \sum_{i=1}^{N} s_i^2$$

But $s_i^2 = l^2$ for both positive as well as negative displacements.

$$\Rightarrow x^2(N) = N l^2 \qquad -(2)$$

$\Rightarrow$ The particle has gone as far as $\sqrt{N}$.

Hence, the particle "spreads" out in space. N here is an indicator of time. It can be seen that the square of the distance travelled by the particle is proportional to the time of travel. This behaviour is identified as "free diffusion".

The continuum diffusion equation can be obtained from random walk by taking the limit of spacing l and time tending to zero.

$P(i, N)$ = probability that the particle is at site i after N steps.

Since there is an equal probability of walking towards +ve or -ve direction,

$$P(i, N) = \frac{1}{2} P(i+1, N-1) + \frac{1}{2} P(i-1, N-1) \quad -(3)$$

If τ is the time for single step walk, then the continuum variables can be written as

$$t = N\tau$$
$$x = il$$

$$\Rightarrow P(x|l, t|\tau) = \frac{1}{2} P(x|l + 1, t|\tau - 1) + \frac{1}{2} P(x|l - 1, t|\tau - 1) \quad -(4)$$

The probability remains unchanged with the walk.

$$a\,P(x, t) = P(ax, t)$$
$$b\,P(x, t) = P(x, bt)$$

where a and b are constants. Using this Eq^n (4) can be re-written as

$$P(x, t) = \frac{1}{2} P(x+l, t-\tau) + \frac{1}{2} P(x-l, t-\tau) \quad -(5)$$

$$\Rightarrow \frac{P(x, t) - P(x, t-\tau)}{2\tau} = \frac{1}{2\tau} \{ P(x+l, t-\tau) + P(x-l, t-\tau) - 2P(x, t-\tau) \} \quad -(6)$$

In the limit $\tau \to 0$, Eq^n (6) defines a derivative.

Using Taylor series expansion,

$$p(x, t-\tau) \approx p(x,t) - \frac{\partial p(x,t)}{\partial t}\tau$$

$$p(x \pm \delta, t-\tau) \approx p(x,t) \pm \frac{\partial p(x,t)}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 p(x,t)}{\partial x^2}\delta^2 - \frac{\partial p(x,t)}{\partial t}\tau$$

Using the above, Eq^n (6) can be written as

$$\frac{p(x,t) - p(x,t) + \frac{\partial p(x,t)}{\partial t}\tau}{\tau} \approx$$

$$p(x,t) + \frac{\partial p(x,t)}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 p(x,t)}{\partial x^2}\delta^2 - \frac{\partial p(x,t)}{\partial t}\tau$$

$$+ p(x,t) - \frac{\partial p(x,t)}{\partial x}\delta + \frac{1}{2}\frac{\partial^2 p(x,t)}{\partial x^2}\delta^2 - \frac{\partial p(x,t)}{\partial t}\tau$$

$$- 2p(x,t) + 2\frac{\partial p(x,t)}{\partial t}\tau$$

$$\Rightarrow \frac{\partial p(x,t)}{\partial t} \approx \frac{\delta^2}{2\tau}\frac{\partial^2 p(x,t)}{\partial x^2}$$

The above approximation becomes exact as $\tau \to 0$ and $\delta \to 0$. $\delta^2/2\tau$ is defined as the diffusion coefficient, D.

$$\frac{\partial p(x,t)}{\partial t} = D\frac{\partial^2 p(x,t)}{\partial x^2} \qquad - (7)$$

Eq^n (7) can be identified as the parabolic PDE known as the heat equation or diffusion equation.

$P(x,t)$ satisfies the previous equation with

$$P(x,t) = \frac{N}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \qquad - (8)$$

Again, Eq^n (8) can be seen as a Gaussian. Hence, diffusion results in a Gaussian distribution of the molecules in space.

Now using $D = l^2/2\tau$ and $t = N\tau$, we can rewrite the expression for $x^2(t)$

$$x^2(t) = l^2 N$$

$$= D \times 2\tau \times \frac{t}{\tau}$$

$$\Rightarrow x^2(t) = 2Dt \qquad - (9)$$

Eq^n (9) is the famous Einstein relation. In 3-D

$$\frac{\partial P}{\partial t}(x,y,z,t) = D \nabla^2 P(x,y,z,t) \qquad - (10)$$

with the Einstein relation as

$$R^2(t) = 6Dt$$

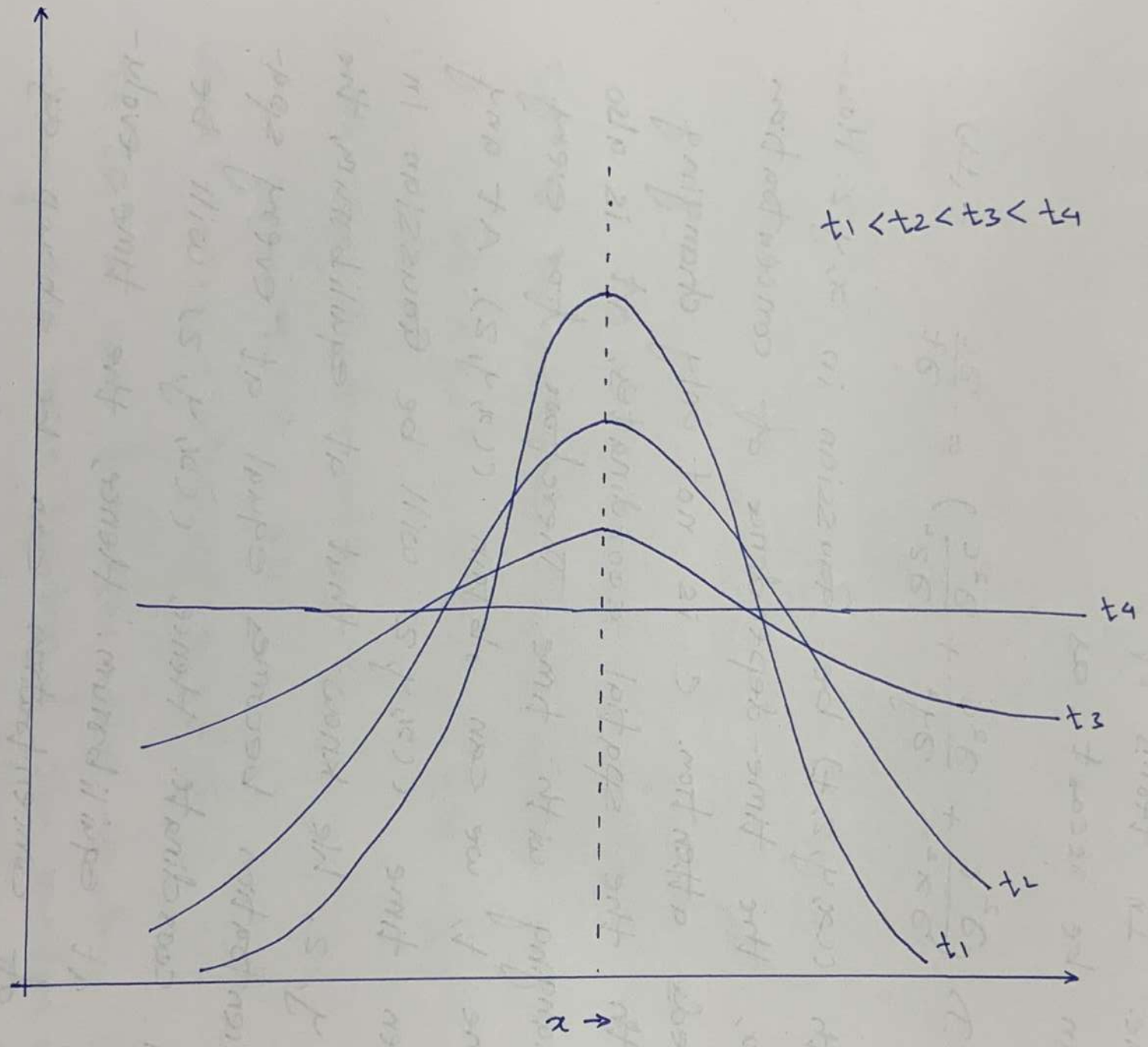
where $R^2(t) = x^2(t) + y^2(t) + z^2(t)$

It can be seen from the above equations that although the mean position of the random walker is at zero, the walker "diffuses" out at a distance which is not proportional to the time rather square of the distance is proportional to the time.

The probability distribution is not an observable. Rather, concentration, which governs the probability distribution, is an observable. In terms of concentration, Eqn (10) can be recast as

$$D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) = \frac{\partial c}{\partial t} \qquad -(11)$$

with $c(x, y, z, t)$ be Gaussian in x, y, z. However, the time-dependence of concentration needs attention. c is not only changing with the spatial coordinates, it is also changing with time. Therefore, for every time t, we can obtain $c(x, y, z)$. At any given time $c(x, y, z)$ will be Gaussian in x, y, z. We know that at equilibrium, the concentration becomes equal at every spatial coordinate. Hence, $c(x, y, z)$ will be flat at equilibrium. Hence, the time-evolution of concentration can be shown as the one in the following figure.


$t_1 < t_2 < t_3 < t_4$
C
x
t_4
t_3
t_2
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Energy calculations using classical methods

The discussion for calculation of energies undertaken till now used the principles of quantum mechanics and required the solution of many-body schrödinger equation. Such calculations are extremely time and resource consuming. Another class of methods often used to describe physical properties of a system are molecular mechanics methods also known as force field methods. These methods are based on the fact that a large molecule can be considered to be a combination of smaller units. Each smaller unit exhibits a behaviour which is dependent upon the identity of the unit itself as well as the other units it is linked to. Energy for each unit is the calculated and its contribution is added to the total energy. Therefore, the force fields, unlike quantum methods are not universal but are system dependent.

Force field energy :

A molecule in a classical description is considered to be made of a collection of balls (masses), joined by linkages which are allowed to compress, expand and rotate. The total energy of the system comes from a series of contributions given below.

$$E = E_{str} + E_{bend} + E_{tors} + E_{vdw} + E_{el} + E_{cross} \quad - (1)$$

E_{str} → energy function for stretching a bond between two atoms

E_{bend} → energy function for bending an angle between three atoms

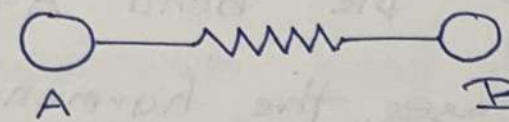
E_{tors} → torsional energy function for rotation around a bond

E_{vdw} and E_{el} → non-bonded interactions

E_{cross} → coupling between the first three terms on RHS.

Stretching energy:

Two atoms in the classical framework are visualized to be connected (bonded) by an elastic spring.



We know from classical mechanics that as the equilibrium position of the atoms is disturbed either by stretching or compression, the energy of the system increases. If R_0 is the equilibrium bond length then the stretching energy can be obtained by a Taylor series expansion around R_0.

$$E_{str}(R^{AB} - R_0^{AB}) = E(0) + \frac{dE}{dR}\Big|_{R_0^{AB}} (R^{AB} - R_0^{AB}) + \frac{1}{2}\left(\frac{d^2E}{dR^2}\right)\Big|_{R_0^{AB}} (R^{AB} - R_0^{AB})^2 \quad -(2)$$

Most often, it is desired to determine the deviation rather than the absolute energy and the derivative is zero about R_0^{AB}

$$\Rightarrow E(0) = dE/dR\,|_{R_0^{AB}} = 0$$

$$\Rightarrow E_{str}(R^{AB} - R_0^{AB}) = k_{AB}(R^{AB} - R_0^{AB})^2$$

$$\Rightarrow E_{str} = k_{AB}(\Delta R)^2 \quad -(3)$$

Eq^n (3) can be identified as the equation of a harmonic oscillator with k_{AB} as the force constant for the bond A-B.

In most cases, the harmonic approximation is good enough and reproduces experimental data. Else, more number of terms are used in Taylor series expansion.

$$E_{str} = k_{AB2}(\Delta R)^2 + k_{AB3}(\Delta R)^3 + \ldots$$

However such expansions may cause wrong limiting behaviours. For example, for bond stretching to infinity, the energy should converge to the bond dissociation energy. A simple function which captures this feature is the Morse potential.

$$E_{Morse}(\Delta R) = D(1 - e^{-\alpha \Delta R})^2 \quad -(4)$$

where $\alpha = \sqrt{\frac{k}{2D}}$

Bending energy:

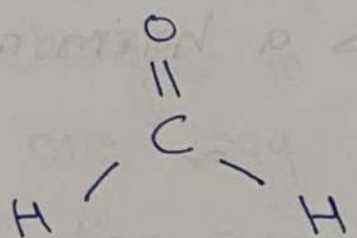
If there is a bond between atoms A and B and there is also a bond between atoms B and C then E_{bend} gives the energy required to change the angle A-B-C. Similar to the equilibrium bond distance, there exists equilibrium bond angle and for small changes in bond angles (positive or negative) second order terminated Taylor series expansion about the equilibrium bond angle gives the harmonic approximation.

$$E_{bend}(\theta^{ABC} - \theta_0^{ABC}) = k^{ABC}(\theta_A^{ABC} - \theta_0^{ABC})^2$$

$$\Rightarrow E_{bend} = k^{ABC}(\Delta\theta)^2 \qquad -(5)$$

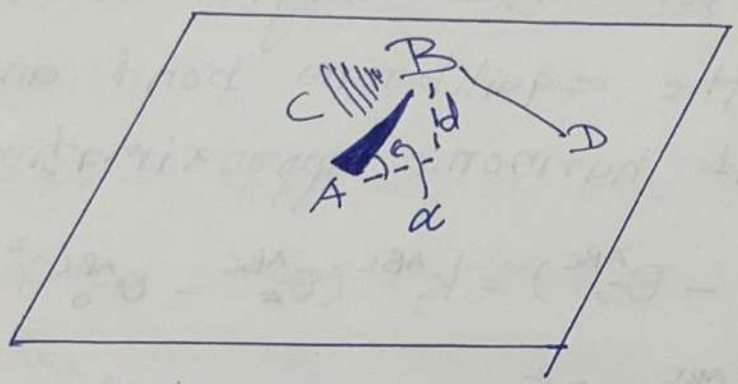
For most physically relevant systems, the bending energy is well-approximated by harmonic approximation.

Now consider the following case.



In this case, the molecular arrangement

is planar. The sum of angles between the two H-C-O angles and the H-C-H angle must be 360°. However, keeping this constraint of 360; the central atom (carbon in this case) may come out of the plane. Therefore it becomes important to define what is called the out-of-plane bending energy. Consider the following molecule.



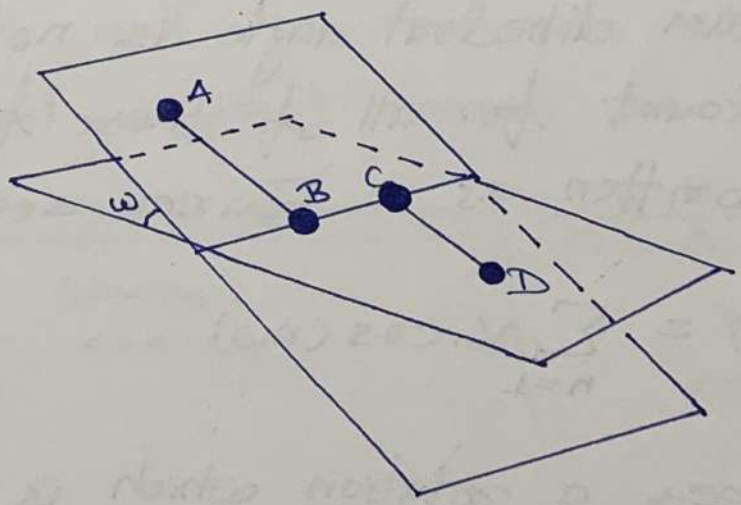
The atom B is the central atom and it comes out of the A-C-D plane which is characterized by the angle α and the distance d as shown. The equilibrium values of α and d are both zero. The out-of-plane energy function can be written as a harmonic term as

$$E_{oop}(\alpha) = k^B \alpha^2 \quad \text{or}$$

$$E_{oop}(d) = k^B d^2 \qquad -(6)$$

Torsional energy:

Consider four atoms A-B-C-D. Two planes can be defined for this system containing the atoms A-B-C and the atoms B-C-D. The angles between these two planes is called the dihedral angle. In this system the bonded atoms are A-B, B-C, C-D. The system is shown below. The dihedral angle is ω. As can be observed from the figure, on changing ω,



(a) all bond distances remain constant

(b) all bond angles remain constant

Still, due to changes in relative positions of the atoms, one may expect changes in the energies of the system. Hence, it is necessary to define torsional energy.

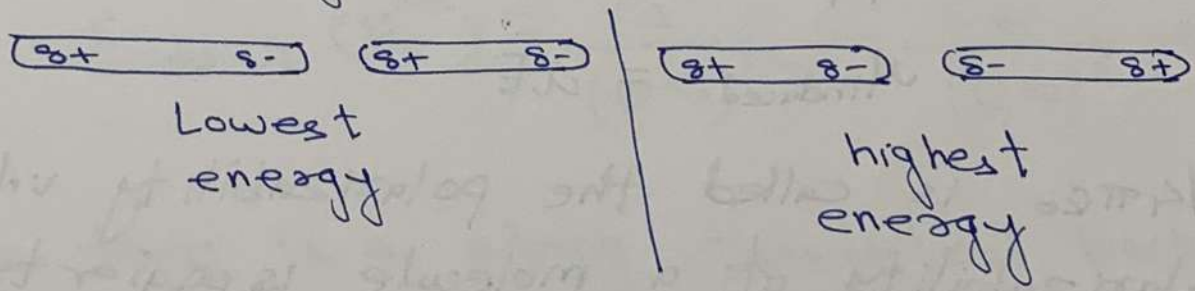
Unlike stretching and bending energy functions, torsional energy function needs to have periodicity. This is because on rotation of the dihedral angle by 360°, the original configuration of the molecule is regained and hence, the energy must be periodic. Also, unlike the previous two energy terms where the distortions are allowed to be small, large torsions are indeed observed in molecular system and hence, Taylor series expansion of the torsional energy about the equilibrium dihedral angle is not a good idea. To account for all of these factors, E_{tors} is written as a Fourier series.

$$E_{tors}(\omega) = \sum_{n=1} V_n \cos(n\omega) \qquad -(7)$$

$n=1$ describes a rotation which is periodic by 360°, $n=2$ term is periodic by 180°, $n=3$ term is periodic by 120° and so on. The value of V_n signify the energy required for rotation. For e.g. single bond torsion is easier when compared to double bond torsion and hence, the corresponding values of V_n will differ.

van der Waals energy:

E_{vdw} is termed as the van der Waals energy term which is a non-bonded interaction energy term. Consider any two non-bonded atoms in a molecule. At large distances, they do not feel each other's presence and hence E_{vdw} equals zero. As the atoms come closer, slight attraction is developed between them. For two dipolar molecules of dipole moments μ_1 and μ_2, the two states of lowest and highest energy are as shown.

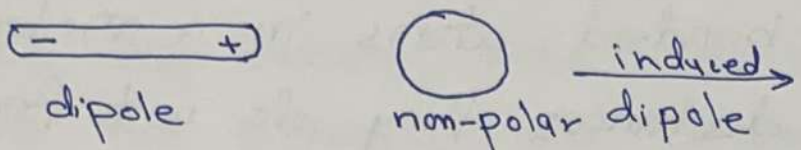


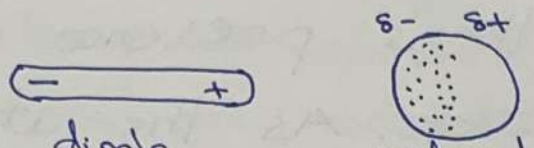
The energy of the dipole is given as

$$u_{dd}(r) = -\frac{2\mu_1^2\mu_2^2}{(4\pi\epsilon_0)^2(3k_BT)}\frac{1}{r^6} \quad -(8)$$

If one of the molecules has a permanent dipole moment while the other one does not, then the polar molecule

can "induce" a dipole in the non-polar molecule. This happens due to re-distribution of electron density in presence of a dipole.





The ability to get polarized in an electric field is called polarizability. If E is the applied electric field then

$$\mu_{induced} = \alpha E$$

$\alpha/4\pi\epsilon_0$ is called the polarizability volume. Polarizability of a molecule is proportional to its polarizability volume.

The energy for a dipole-induced dipole is given as

$$u(r) = \frac{-\mu_1^2 \alpha_2}{(4\pi\epsilon_0)^2 r^6} - \frac{\mu_2^2 \alpha_1}{(4\pi\epsilon_0)^2 r^6} \quad - (9)$$

where μ_1 is the dipole moment and μ_2 is the induced dipole moment. The second term on RHS is called London dispersion.

It can be seen from Eq^{n}s (8) and (9) that the attractive potentials vary as r^{-6}. At very small distances, the electron clouds start interacting resulting in repulsive potentials. Therefore, we need a term which quickly rises (due to very small interatomic distances) increasing the energy and which asymptotically goes to zero at large distances. A function which satisfies these requirements is the Lennard-Jones (LJ) potential which is given as

$$E_{vdw\text{-}LJ}(R^{AB}) = \frac{C_1}{(R^{AB})^{12}} - \frac{C_2}{(R^{AB})^{6}} \quad -(10)$$

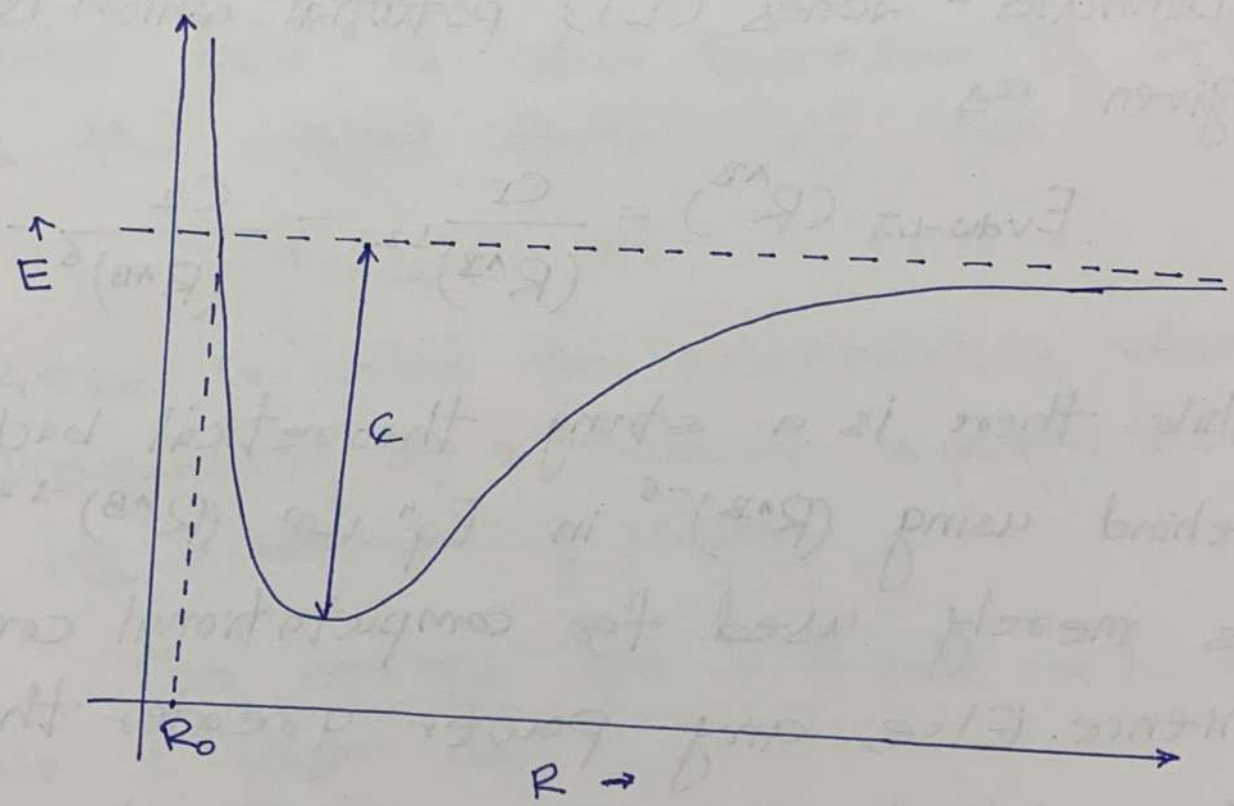
While there is a strong theoretical backing behind using $(R^{AB})^{-6}$ in Eq^n (10), $(R^{AB})^{-12}$ is merely used for computational convenience. Else, any power greater than 6 would do. Eq^n (10) is commonly written as

$$E_{vdw\text{-}LJ}(R^{AB}) = 4\epsilon\left\{\left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^{6}\right\} \quad -(11)$$

ϵ → depth of the potential well. Its value signifies how strongly are molecules interacting (attracting)

R_0 → distance at which $E_{vdw-LJ}(R^{AB}) = 0$. It is also a measure of the size of the molecule.

Clearly, ϵ and R_0 are dependent upon the identity of the molecular species. The general nature of the LJ potential is as shown below.



While LJ potential is the most popular one, there are other functions, e.g. Buckingham potential, to describe non-bonded interactions.

Electrostatic energy :

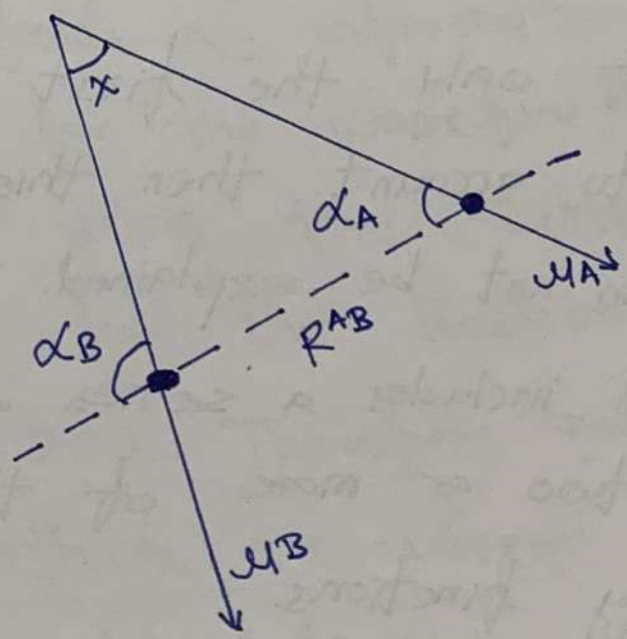
As seen before, internal re-distribution of charges occurs in molecules resulting in non-bonded interactions. Therefore it is possible to assign partial charges to the atoms. The interaction between point charges is given by the Coulomb potential.

$$E_{el}(R^{AB}) = \frac{Q^A Q^B}{\epsilon R^{AB}} \qquad -(12)$$

Alternatively, the electrostatics description can be made using bond dipole description. In this,

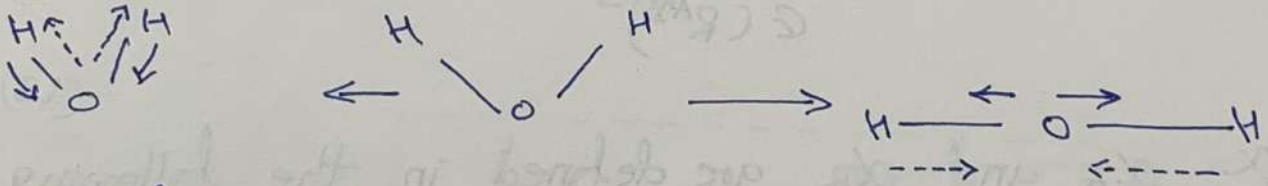
$$E_{el}(R^{AB}) = \frac{\mu^A \mu^B}{\epsilon (R^{AB})^3} (\cos\chi - 3\cos\alpha_A \cos\alpha_B) \qquad -(13)$$

χ, α_A and α_B are defined in the following figure.



Cross terms :

Let us consider an example of water molecule. The equilibrium bond distance is 0.96 Å & the equilibrium bond angle is 104.5°. When the angle is compressed to 90°, the equilibrium bond distance enlarges. Conversely, when the angle is enlarged, the hydrogens ~~go farther apart~~ come closer. So it can be seen that a change in angle is resulting in a change in bond distance. Therefore a coupling of stretching energy and bending energy can be expected.



⟶ for angle

---> for bond distance

If only the first five terms are taken into account then this coupling of bonded terms can not be explained. Therefore E cross in general includes a series of terms that couple two or more of the bonded terms of energy functions.

The examples of cross terms are as given in the following relations.

$$E_{str/bend} = k^{ABC}(\theta^{ABC} - \theta_o^{ABC})\{(R^{AB} - R_o^{AB}) - (R^{BC} - R_o^{BC})\}$$

$$E_{str/str} = k^{ABC}(R^{AB} - R_o^{AB})(R^{BC} - R_o^{BC})$$

$$E_{bend/bend} = k^{ABCD}(\theta^{ABC} - \theta_o^{ABC})(\theta^{BCD} - \theta_o^{BCD})$$

$$E_{str/tors} = k^{ABCD}(R^{AB} - R_o^{AB})\cos(n\omega^{ABCD})$$

$$E_{bend/tors} = k^{ABCD}(\theta^{ABC} - \theta_o^{ABC})\cos(n\omega^{ABCD})$$

$$E_{bend/tors/bend} = k^{ABCD}(\theta^{ABC} - \theta_o^{ABC})(\theta^{BCD} - \theta_o^{BCD})\cos(n\omega^{ABCD})$$

A comparison of method for calculation of energy of a molecular system and that by force fields will quickly indicate the problem of using force fields. No information is required to solve for the wavefunction of a molecular system using the Schrödinger equation except for the location of the nuclei and electrons. Therefore, quantum mechanics-based methods are universal. In contrast, one needs to determine all the para-

parameters involved in the force field e.g. k^{AB}, k^{ABC} and so on. Not only that these are unknown, they are also system-dependent. Therefore one needs to carry out force field "parameterization" before one can employ the force field-based techniques to calculate energies and other physical properties. These parameters are infact obtained by curve-fitting the results obtained from quantum method-based calculations.

Another problem with the use of force fields is that they completely disregard the electronic structure of the molecular system. As can be seen from the previous discussion, reference is only made to the masses of the nuclei. Therefore, only physical properties of the systems can be determined using force field methods. For systems involving chemical reactions, quantum mechanics based methods must be used. Nevertheless, force fields have been used successfully in molecular dynamics simulations and Monte-Carlo simulations to successfully describe physical processes.