Probability

If one gets outcome i N_i times in N tries, then the probability $P(i)$ is the limit

$$P(i) = \lim_{N \to \infty} \frac{N_i}{N}.$$

Note $0 \leq P(i) \leq 1$.

$$P(i \text{ or } j) = P(i) + P(j) \quad \text{for } i \neq j.$$

$$\sum_{\text{all } i} P(i) = \sum_{\text{all } i} \frac{N_i}{N} = \frac{1}{N} \sum_i N_i = \frac{N}{N} = 1.$$

These are the rules for distinct discrete outcomes.

Now suppose that x is a continuous real variable.

Suppose the possible values of x are all real numbers $a \leq x \leq b$.

We can split the interval $[a, b]$ into H bins of size

$$dx = \frac{b-a}{H}$$

where H is a huge number.

We use the same definition where now the index i labels the bins.

Bin 1 is the interval $[a, a+dx]$.

Bin 2 " " " $[a+dx, a+2dx]$.

Bin H " " " $[b-dx, b]$.

We say

$$P(i) = \lim_{N \to \infty} \frac{N_i}{N}$$

but now these $P(i)$'s are proportional to the size dx of the bins.

So to avoid reference to the size of the bins, we set for x in bin i

$$P(x)\,dx = \left(\lim_{i \to \infty} \frac{N_i}{N}\right) \doteq P(i).$$

Now the probability distribution

$$P(x) = \frac{P(i)}{dx}$$

is no longer bounded by unity. For instance, if all the x_i's were to fall in the first bin, then $P(1)$ would be 1 and $P(x)$ would be

$$P(x) = \frac{P(1)}{dx} = \frac{1}{dx} \quad \text{for } a \leq x \leq a + dx$$

and

$$P(x) = \frac{0}{dx} = 0 \quad \text{for } x > a + dx.$$

So $P(x)$ would be big for $a \leq x \leq a + dx$ if dx is small.

$$\int_a^b P(x)\,dx = \sum_i P(i) = \sum_i \frac{N_i}{N} = \frac{\sum_i N_i}{N} = \frac{N}{N} = 1$$

So the probability distribution

$$P(x)$$

is normalized to unity over the interval of possible outcomes.

The uniform distribution on $[a,b]$ is

$$P(x) = \frac{1}{b-a} \quad \text{for} \quad a \le x \le b$$

$$= 0 \quad \text{for} \quad x < a \text{ or } x > b.$$

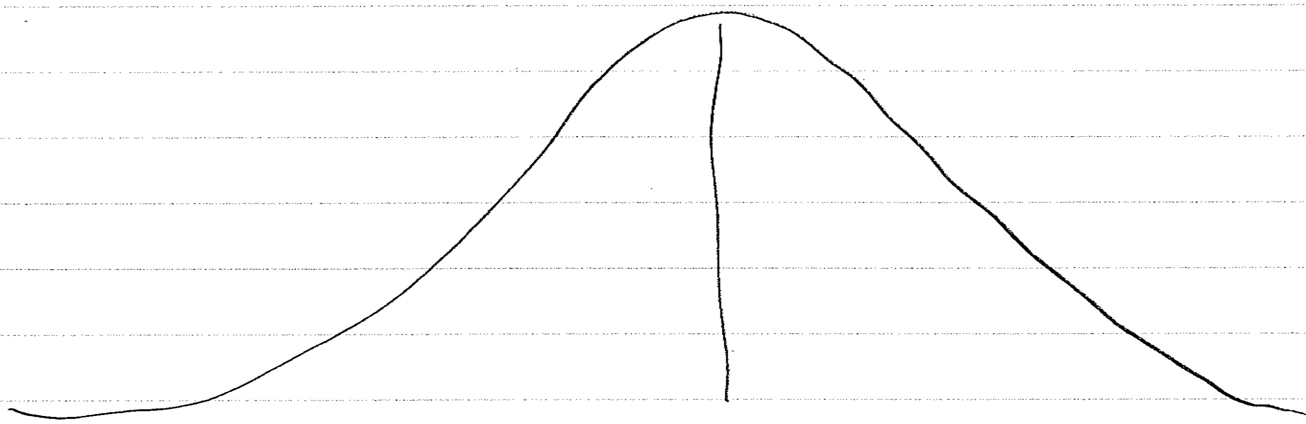
The gaussian distribution is

$$P(x) = A\, e^{-(x-x_0)^2/2\sigma^2}$$

where A and σ are positive numbers and x_0 is a possible value of the real variable x.

The interval now runs from

$-\infty$ to $+\infty$.



What's A? First note that

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, e^{-x^2-y^2} = \int_0^{\infty} dr\, 2\pi r\, e^{-r^2} = \pi \int_0^{\infty} du\, e^{-u}$$

$$= \pi \left[-e^{-u} \right]_0^{\infty} = \pi \left(0 - (-1) \right) = \pi$$

So

$$\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}\,.$$

So to normalize the probability distribution

$$P(x) = A\, e^{-(x-x_0)^2/2\sigma^2}$$

we compute

$$1 = A \int_{-\infty}^{\infty} dx\, e^{-(x-x_0)^2/(2\sigma^2)}$$

by setting $y = (x-x_0)/(\sigma\sqrt{2})$ so that $dy = dx/(\sigma\sqrt{2})$. Then $dx = \sigma\sqrt{2}\, dy$ and

$$1 = A\sigma\sqrt{2} \int_{-\infty}^{\infty} dy\, e^{-y^2} = A\sigma\sqrt{2}\sqrt{\pi}$$

whence

$$A = \frac{1}{\sigma\sqrt{2\pi}}.$$

So

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

is the normalized probability distribution.

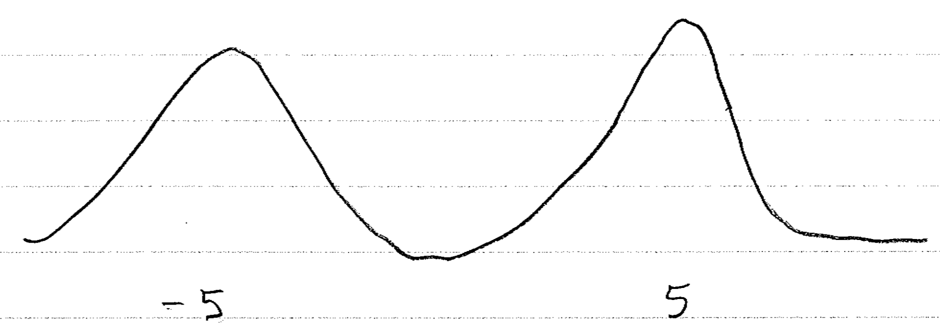
The mean is

$$\langle x \rangle = \sum_i x_i P(i) \qquad \text{discrete}$$

$$= \int dx \; x \; P(x) . \qquad \text{continuous.}$$

The mean is the average. It is also called "the expected value" or "the expectation value," (sic).

The mean need not be the most probable value. For instance,



the most probable value would be $x=5$, but the mean $\langle x \rangle$ would be tiny, near $x=0$, and the probability distribution $P(x)$ would have the small value $P(\langle x \rangle)$ at the mean $\langle x \rangle$.

The mean of $f(x)$ is

$$\langle f \rangle = \langle f(x) \rangle = \sum_i f(x_i)\, P(i) \qquad \text{discrete}$$

$$= \int dx\, f(x)\, P(x) \qquad \text{continuous.}$$

If $f(x) = c$ is a constant,

then

$$\langle f(x) \rangle = \langle c \rangle = \int dx\, c\, P(x) = c.$$

So

$$\langle \langle f \rangle \rangle = \langle f \rangle.$$

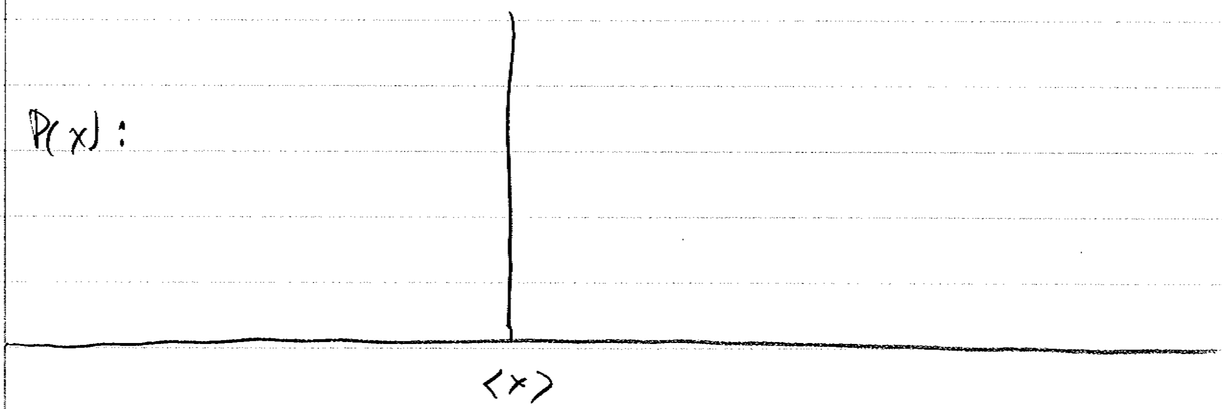
The rms deviation is

$$\text{rmsd} = \sqrt{\langle (x - \langle x \rangle)^2 \rangle}$$

$$= \left(\int dx\, (x - \langle x \rangle)^2\, P(x) \right)^{1/2}$$

where $\langle x \rangle = \int dx\, x\, P(x)$ is the mean.

If the rms deviation (rmsd) is zero, then the probability distribution $P(x)$ must be concentrated at the mean $\langle x \rangle$.



Some use Dirac's notation $P(x) = \delta(x - \langle x \rangle)$ for this case.

The square of the rmsd is the <u>variance</u>.

Note that

$$(\text{rmsd})^2 = \int dx \, (x - \langle x \rangle)^2 \, P(x)$$

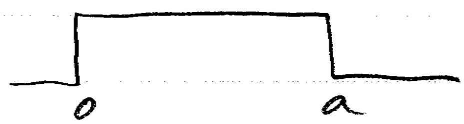
$$\text{variance} = \int dx \left(x^2 - 2x\langle x \rangle + \langle x \rangle^2\right) P(x)$$

$$\text{variance} = \langle x^2 \rangle - 2\langle x \rangle^2 + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 .$$

The uniform distribution $P(x)$ on the interval $[0,a]$ is

$$P(x) = \frac{1}{a} \quad \text{for} \quad 0 \le x \le a$$

and $P(x) = 0$ otherwise. What is the variance or rmsd? Since $P(x)$ is uniform



, the mean must be $a/2$

$$\langle x \rangle = \int_0^a dx \; x \, P(x) = \int_0^a dx \; \frac{x}{a}$$

$$= \frac{1}{a} \int_0^a dx \; x = \frac{1}{a} \left[\frac{x^2}{2} \right]_0^a$$

$$= \frac{a^2}{2a} = \frac{a}{2} \quad \text{as expected.}$$

So $\langle x \rangle = a/2$, and the variance is

$\mathrm{var} = \langle x^2 \rangle - \langle x \rangle^2$. We need $\langle x^2 \rangle$:

$$\langle x^2 \rangle = \int_0^a dx \; x^2 \, P(x) = \frac{1}{a} \int_0^a dx \; x^2 = \frac{1}{a} \left[\frac{x^3}{3} \right]_0^a = \frac{a^2}{3}.$$

So the square of the variance is

$$\text{var} = \langle x^2\rangle - \langle x\rangle^2 = \frac{a^2}{3} - \frac{a^2}{4} = \frac{a^2}{12}.$$

What is the variance for the gaussian distribution

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}} \quad ?$$

Clearly, the mean $\langle x\rangle$ is x_0

$$\langle x\rangle = \int_{-\infty}^{\infty} dx\ x\ P(x) = \int_{-\infty}^{\infty} dx\ \frac{x}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

as we can prove by adding and subtracting x^0

$$\langle x\rangle = x_0 + \int_{-\infty}^{\infty} dx\ \frac{x}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}} - x_0$$

$$= x_0 + \int_{-\infty}^{\infty} dx\ \frac{x-x_0}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

since $\int_{-\infty}^{\infty} dx\, P(x) = 1.$

Let $u(x) = \frac{(x-x_0)^2}{2\sigma^2}$. Then

we have

$$\frac{du}{dx} = \frac{x-x_0}{\sigma^2}$$

and so

$$\langle x \rangle = x_0 + \int_{-\infty}^{\infty} dx \frac{\sigma}{\sqrt{2\pi}} \frac{du(x)}{dx} e^{-u(x)}$$

$$= x_0 + \frac{\sigma}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx \quad u'(x)\, e^{-u(x)}$$

$$= x_0 + \frac{\sigma}{\sqrt{2\pi}} \left[-e^{-u(x)} \right]_{-\infty}^{\infty} = x_0.$$

So $\langle x \rangle = x_0$ as expected.

We could compute $\langle x^2 \rangle$,

but it is easier to compute the

variance directly.

Since x_0 is the mean, the variance is by definition

$$\text{variance}\,(x) = \int_{-\infty}^{\infty} dx \quad (x - x_0)^2 \; P(x)$$

$$= \int_{-\infty}^{\infty} dx \;\; \frac{(x - x_0)^2}{\sigma\sqrt{2\pi}} \; e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

We now change variables as before setting $\quad y = \dfrac{x - x_0}{\sigma\sqrt{2}} \quad$ so that

$$e^{-\frac{(x-x_0)^3}{2\sigma^2}} = e^{-y^2}$$

$$(x - x_0)^2 = 2\sigma^2 y^2$$

$$dy = \frac{dx}{\sigma\sqrt{2}} \qquad dx = \sigma\sqrt{2}\, dy$$

Putting these together, we find

$$\text{variance}(x) = \int_{-\infty}^{\infty} dx \; \frac{(x-x_0)^2}{\sigma\sqrt{2\pi}} \, e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

$$= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} dy \; \sigma\sqrt{2} \; 2\sigma^2 y^2 \, e^{-y^2}$$

$$= \frac{2\sigma^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} dy \; y^2 \, e^{-y^2}$$

Let
$$I(b) = \int_{-\infty}^{\infty} dy \; e^{-by^2}.$$

With $z = \sqrt{b}\, y$, $dz = \sqrt{b}\, dy$, $dy = dz/\sqrt{b}$

and
$$I(b) = \frac{1}{\sqrt{b}} \int_{-\infty}^{\infty} dz \; e^{-z^2} = \frac{\sqrt{\pi}}{\sqrt{b}} = \sqrt{\frac{\pi}{b}}$$

since we already did the integral

$$\int_{-\infty}^{\infty} dx \; e^{-x^2} = \sqrt{\pi}.$$

So

$$\sqrt{\frac{\pi}{b}} = I(b) = \int_{-\infty}^{\infty} dy \; e^{-by^2}.$$

Differentiate both sides with respect to b

$$\frac{d}{db} \sqrt{\pi} \; b^{-1/2} = \sqrt{\pi} \left(-\frac{1}{2}\right) b^{-3/2} = -\frac{1}{2} \sqrt{\frac{\pi}{b^3}}$$

$$= \frac{d}{db} \int_{-\infty}^{\infty} dy \; e^{-by^2} = \int_{-\infty}^{\infty} dy \; \frac{d}{db} e^{-by^2}$$

$$= - \int_{-\infty}^{\infty} dy \; y^2 \; e^{-by^2}$$ so

by this trick, we get

$$\int_{-\infty}^{\infty} dy \; y^2 \; e^{-by^2} = \frac{1}{2} \sqrt{\frac{\pi}{b^3}}$$

or setting $b = 1$

$$\int_{-\infty}^{\infty} dy \; y^2 \; e^{-y^2} = \frac{\sqrt{\pi}}{2}.$$

The variance of the gaussian

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

is

$$\text{variance}(x) = \frac{2\sigma^2}{\sqrt{\pi}}\,\frac{\sqrt{\pi}}{2} = \sigma^2.$$

Since the variance is the rmsd squared, we also have

$$\text{rmsd} = \sigma$$

for the gaussian $P(x)$.

Probabilities for exclusive events add. The probability that x is either less than 1 or greater than 2 is

$$P(x<1 \text{ or } x>2) = P(x<1) + P(x>2)$$

$$= \int_{-\infty}^{1} dx\, P(x) + \int_{2}^{\infty} dx\, P(x).$$

But the probability that $x > 1$ or $y > 2$ need not be the sum

$$P(x>1, y>2) \overset{?}{=} P(x>1) + P(y>2).$$

because an event can have $x > 1$ and $y > 2$.

If two variables x and y are independent, then their joint probability distribution is the product

$$P(x,y) = P(x)\, P(y)$$

and it is properly normalized

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\; P(x,y) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\; P(x)\, P(y)$$

$$= \int_{-\infty}^{\infty} dx\, P(x) \int_{-\infty}^{\infty} dy\, P(y) = 1 \cdot 1 = 1.$$

Review: Discrete events

$$P(i) = \lim_{N \to \infty} \frac{N_i}{N}.$$

Continuous variable x

$$P(x)\,dx = \lim_{N\to\infty} \frac{N_i}{N}, \qquad N_i \text{ is number in } [x - \tfrac{dx}{2}, x + \tfrac{dx}{2}].$$

$$1 = \int P(x)\,dx = \sum_i P(i).$$

Gaussian distribution

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}}\, e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

has mean

$$\langle x \rangle = \int dx \; x \; P(x) = x_0$$

and variance

$$\langle (x - x_0)^2 \rangle = \langle x^2 \rangle - x_0^2$$

$$= \int dx\,(x^2 - x_0^2)\,P(x) = \sigma^2.$$

Ex.
$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2}$$

$$P(y) = \frac{1}{\sigma\sqrt{2\pi}} e^{-y^2/2\sigma^2}$$

$$P(x,y) = P(x)\,P(y) = \frac{1}{2\pi\sigma^2} e^{-\frac{x^2+y^2}{2\sigma^2}}$$

let $r^2 = x^2 + y^2$ then

$$P(x,y) = \frac{1}{2\pi\sigma^2} e^{-\frac{r^2}{2\sigma^2}}$$

The area of the ring is $2\pi r\,dr$, so

$$P(r)\,dr = \frac{1}{2\pi\sigma^2} e^{-\frac{r^2}{2\sigma^2}} 2\pi r\,dr$$

$$= \frac{r}{\sigma^2} e^{-r^2/2\sigma^2} dr$$

so probability x, y in ring at r of width dr,

$\boxed{3D}$

$$P(2) = \frac{1}{6}\cdot\frac{1}{6} = \frac{1}{36}$$

$6 = 5+1 = 1+5 = 4+2 = 2+4 = 3+3$ So

$$P(6) = \frac{5}{6\cdot 6} = \frac{5}{36}$$

$$P(12) = \frac{1}{36}.$$

$\boxed{3E}$ $$P(r>R_0) = \int_{R_0}^{\infty} dr \, \frac{r}{\sigma^2} e^{-r^2/2\sigma^2}$$

Let

$$u = r^2/2\sigma^2$$

$$du = r/\sigma^2 \, dr$$

So
$$P(r>R_0) = \int_{u(R_0)}^{\infty} du \, e^{-u} = \left[-e^{-u}\right]_{u(R_0)}^{\infty}$$

$$= e^{-u(R_0)} = e^{-R_0^2/2\sigma^2}.$$

$P(v) = P(v_x)\,P(v_y)\,P(v_z)$

$$= \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{v_x^2}{2\sigma^2}} \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{v_y^2}{2\sigma^2}} \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\frac{v_z^2}{2\sigma^2}}$$

$$= \frac{1}{(2\pi\sigma^2)^{3/2}}\, e^{-\frac{u^2}{2\sigma^2}}$$

where $u^2 = v_x^2 + v_y^2 + v_z^2$.

The volume of the shell is $4\pi u^2 du$, so

$$P(u)\,du = \frac{4\pi u^2}{(2\pi\sigma^2)^{3/2}}\, e^{-u^2/2\sigma^2}\, du$$

$$= \frac{2u^2}{\sigma^3\sqrt{2\pi}}\, e^{-u^2/(2\sigma^2)}\, du$$

$$= \left(\frac{1}{\sqrt{2\pi}\,\sigma}\right)^3 e^{-u^2/(2\sigma^2)}\, 4\pi u^2\, du.$$

Ideal - Gas Law

"Ideal" means that the gas molecules do not interact with each other except to scatter elastically.

$pV = NkT$ is the ideal-gas law

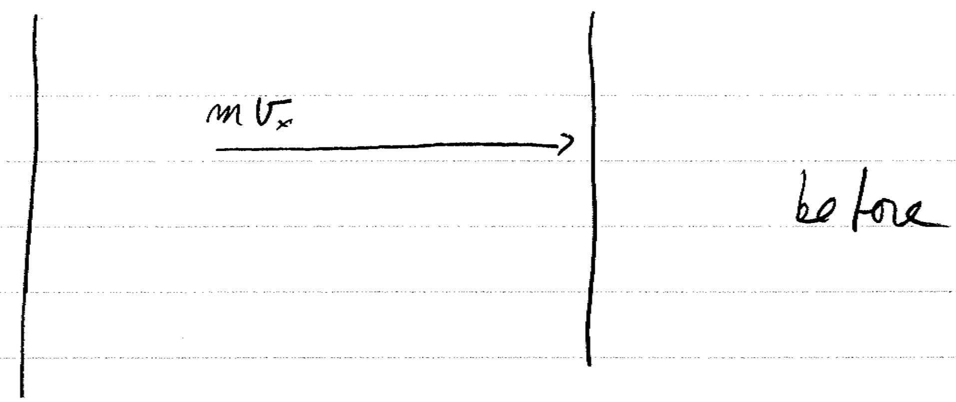
where N is the number of molecules of gas in the volume V at pressure p and temperature T in K. Here $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant

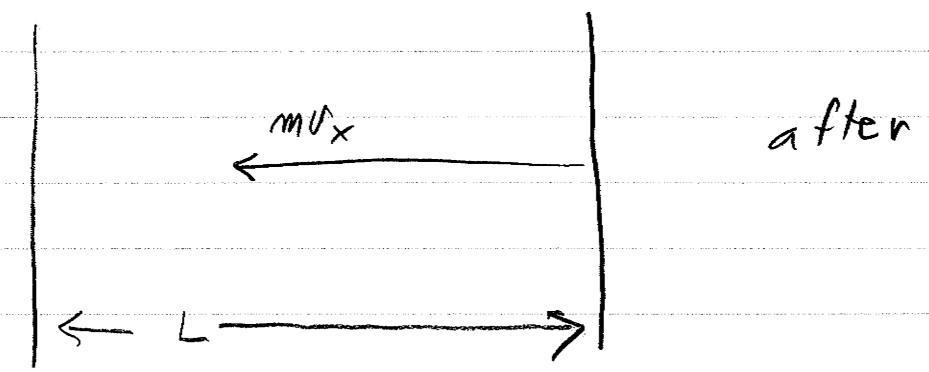
$$kT_r \approx 4.1 \text{ pN nm}$$

where $T_r \approx 295$ is room temperature.

Now $[kT]$ = force $\times$ distance = N m = energy.

Also, $pV = pAL$ and $[p] = \frac{\text{force}}{\text{area}}$, so $[pA]$ = force, so $[pV]$ = energy.





The time between impacts on the right wall is $\Delta t = \frac{2L}{v_x}$. The momentum transferred to the wall by each impact is $\Delta p_x = 2mv_x = 2p_x$.

So the average force due to one molecule of mass m is

$$f = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{(2L/v_x)} = \frac{mv_x^2}{L}.$$

If A is the area of the right wall,

then the pressure on it is

$$p = \frac{f}{A} = \frac{m v_x^2}{LA} \, .$$

If the box is a cube, then $LA = V$,

and we have

$$p = \frac{m v_x^2}{V} \quad \text{for one molecule.}$$

For a cube with N molecules, all of

mass m, all moving at speed v_x

$$pV = N \, m v_x^2 .$$

Since the molecules have different speeds

we take the average

$$\langle pV \rangle = pV = N m \langle v_x^2 \rangle .$$

But the ideal-gas law is

$$pV = NkT.$$

So

$$pV = NkT = Nm\langle v_x^2\rangle.$$

So

$$m\langle v_x^2\rangle = kT.$$

Now

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

and so

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

but surely

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

So $\langle v^2\rangle = 3\langle v_x^2\rangle$ and so

$$m\langle v^2\rangle = 3kT.$$

Thus the mean kinetic energy of a molecule of mass m in an ideal gas at pressure p and temperature T is

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

A mole of air occupies 24 L or $0.024\,m^3$ at atmospheric pressure p_a and room temperature T_r.

At sea level, p_a can lift a column of water about 10m. The force needed to support that column is

$$f = 10\,m\ \rho_{H_2O}\, A\, g$$

where A is the area of the column.

Now $\rho_{H_2O} = \frac{1\,gm}{cm^3} = \frac{10^{-3}\,kg}{(10^{-2}\,m)^3} = 10^3 \frac{kg}{m^3}$.

So

$$p_a = \frac{f}{A} = 10\,m \; \frac{10^3\,kg}{m^3}\, g$$

$$= 10^4 \frac{kg}{m^2} \; \frac{9.8\,N}{kg} \approx 10^5 \frac{N}{m^2}$$

$$= 10^5 \, P_a$$

where on $P_a = \frac{N}{m^2}$ is one Pascal.

So for one mole of air

$$pV = NkT_r$$

and $kT_r = 4.1\,pN\,nm = 4.1\; 10^{-12}\, 10^{-9}\, Nm$

$= 4.1 \times 10^{-21}\, J$ and so

$$NkT_r \approx 6.0 \times 10^{23} \times 4.1 \times 10^{-21} J = 2460\, J.$$

while one mole of air occupies ~~24L~~ $= 0.024\,m^3$ (at STP)

so

$$pV = 10^5 \frac{N}{m^2} \times 0.024\,m^3 = 2400\,J,$$

so this works to the precision of the values we are using.

The molar mass of N is 14 g, so one mole of N_2 is 28 g. So the mass of a single molecule of N_2 is

$$\frac{14\,g}{N_A} = \frac{28\ 10^{-3}\,kg}{6 \times 10^{23}} = 4.7 \times 10^{-26}\,kg.$$

$\boxed{3I}$ $\quad \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k T_r = \frac{3}{2} \times 4.1 \times 10^{-21}\,J$

$$\langle v^2 \rangle = \frac{12.3\ 10^{-21}\,J}{m} = \frac{12.3 \times 10^{-21}\,J}{4.7 \times 10^{-26}\,kg} = 2.62 \times 10^{5}\,\frac{m^2}{s^2}$$

So

$$\bar{u} = \sqrt{\langle v^2 \rangle} = 512\,m/s = 512\,\frac{m}{s}\,\frac{3600\,s}{hr} = 1.84 \times 10^{6}\,\frac{m}{hr}$$

$$= 1840\,\frac{km}{hr} = 1840\,\frac{km}{hr}\,\frac{0.621\,mi}{1\,km} = 1143\,\frac{mi}{hr}.$$

Review: The ideal-gas law says

$$pV = NkT$$

where p is the pressure, V the volume, N the number of molecules, k Boltzmann's constant

$$k = 1.38 \times 10^{-23} \ J/K$$

and T the temperature in K.

Room temperature $T_r \approx 295\,K$ and $kT_r \approx 4.1 \ pN\,nm = 4.1\ 10^{-21}\ J$.

Atmospheric pressure $p_A \approx 10^5\,Pa = 10^5\,N\,m^{-2}$.

The mean kinetic energy of a molecule of an ideal gas at temperature T is

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

where m is the mass of the molecule.

We roughly estimate that the gravitational potential energy of an air molecule at $z = 9\,km$ (top of Everest) is its kinetic energy

$$\Delta U = m g\, 9\,km \approx \frac{1}{2} m \langle v^2 \rangle .$$

$\boxed{3J}$ So $\frac{1}{2} \langle v^2 \rangle \approx g\, 9\,km$

$$\langle v^2 \rangle \approx 9.8 \frac{m}{s^2} \times 18 \times 10^3 m = 1.76 \times 10^5 \frac{m^2}{s^2}$$

So

$$\bar{u} = \sqrt{\langle v^2 \rangle} = \sqrt{17.6 \times 10^4} \frac{m}{s}$$

$$= 4.2 \times 10^2 \frac{m}{s} = 420 \frac{m}{s}.$$

$\boxed{3K}$ $\frac{3}{2} k T_r \approx \frac{3}{2} 4.1 \times 10^{-21} J = 6.15 \times 10^{-21} J \approx \frac{1}{2} m \langle v^2 \rangle$

is the mean kinetic energy of an air molecule at room temperature $T_r \approx 295\,K$.

If a room is 3m high, then

$$\Delta U = m g 3 = 4.7 \times 10^{-26} kg\, 9.8 \frac{m}{s^2}\, 3m = 1.38 \times 10^{-24} J$$

So $\frac{1}{2} m \langle v^2 \rangle$ is 4 500 times bigger.

The air doesn't fall to the floor because Δu is negligible compared to $\frac{1}{2} m\langle v^2\rangle$. We could make it fall by dropping the temperature to below 70 K. Then the air molecules would stick together, forming a liquid on the floor.

How about a particle of dirt that has the mass of a 50 μm cube of water?

Now $L = 50\ 10^{-6}\ m = 50\ 10^{-4}\ cm$ so

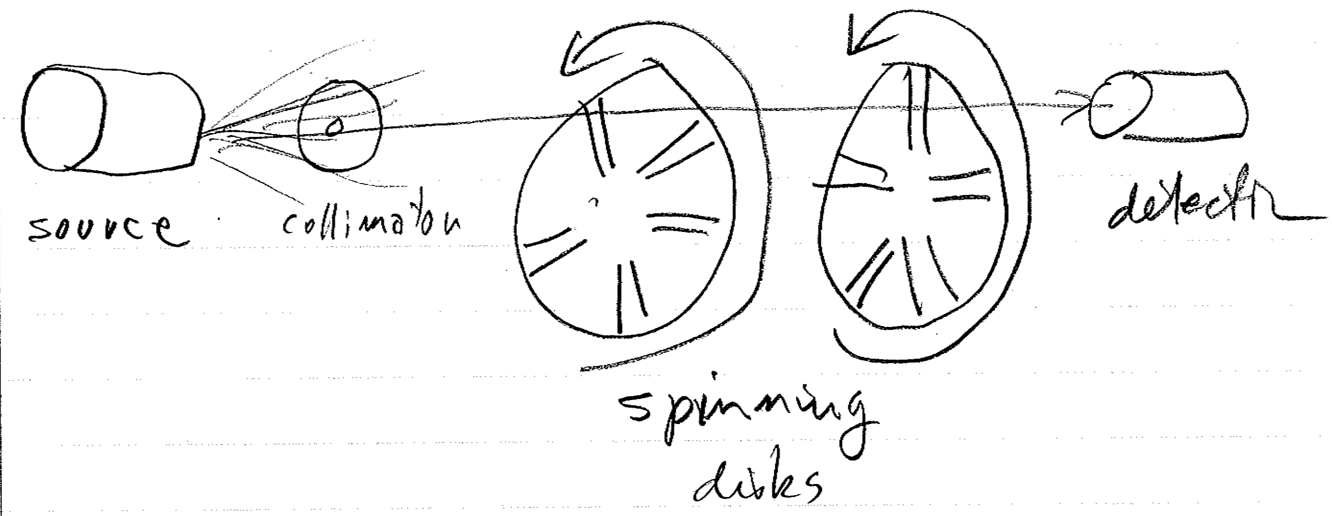
$$V = (5 \times 10^{-3})^3\ cm^3 = 125 \times 10^{-9}\ cm^3$$

so

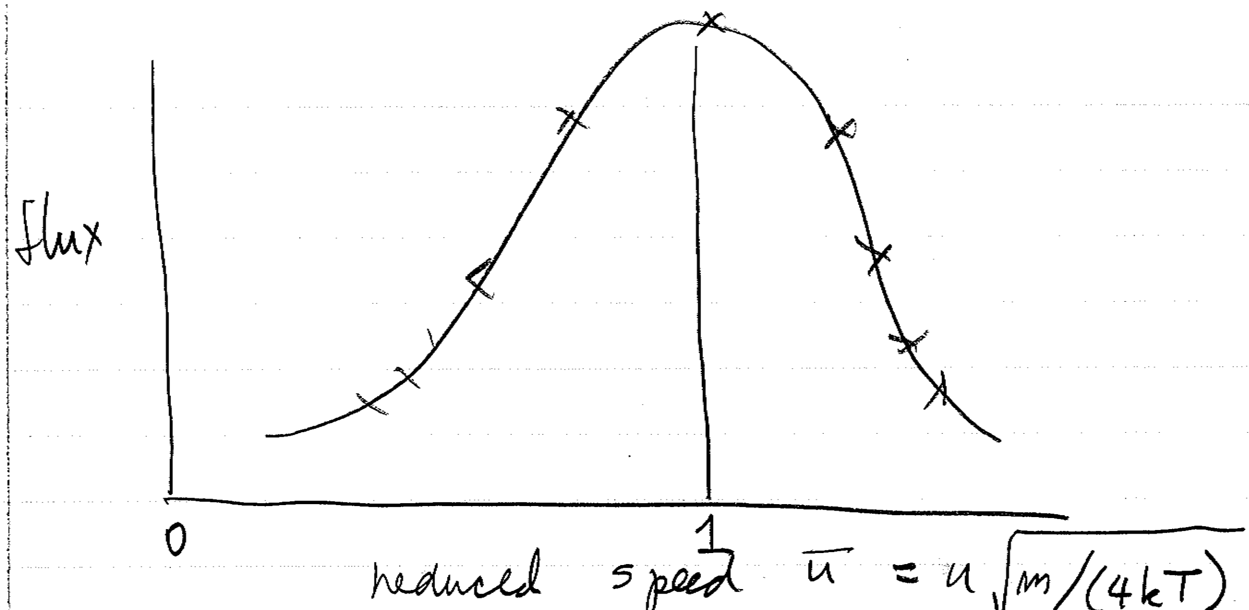
$$m = 1.25 \times 10^{-7}\ g = 1.25 \times 10^{-10}\ kg.$$

Now $\Delta U = mgh = 1.25 \times 10^{-10}\ kg\ 9.8 \frac{m}{s^2}\ 3\ m$

$= 3.68 \times 10^{-9}\ J$ which is more than 10^{10} times the available thermal energy kT_r, so the dirt particle falls to the floor.



A gas of molecules escapes from a hole in the source and passes thru a hole in a disk. The holes define the direction of the velocity of the molecules. Their speeds are determined when they pass thru two slits in two rotating disks. The flux of molecules with the well-defined velocity $\vec{v}$ is measured by the detector.



The data fall on the theoretical curve for all atoms and molecules of different mass m at various temperatures T. This Boltzmann distribution fits all data with <u>no</u> adjustable parameters.

The velocity $\vec{v}$ of any particular molecule changes as it hits other molecules, but the probability distribution $P(\vec{v})$ remains fixed at a given temperature T.

The Boltzmann distribution $P(v_x)$:

We expect that

$$P(v_x) \to 0 \quad \text{as} \quad |v_x| \to \infty$$

We expect that

$$P(-v_x) = P(v_x).$$

We expect that

$$\langle v_x \rangle = 0, \quad \text{since no wind blows.}$$

We expect that

$$\sigma_x^2 = \langle (v_x - \langle v_x \rangle)^2 \rangle = \langle v_x^2 \rangle - \langle v_x \rangle^2$$

$$= \langle v_x^2 \rangle,$$

We know that

$$\langle v_x^2 \rangle = \frac{1}{3} \langle \vec{v}^2 \rangle \quad \& \quad \frac{1}{2} m \langle \vec{v}^2 \rangle = \frac{3}{2} kT$$

So

$$\sigma_x^2 = \langle v_x^2 \rangle = \frac{kT}{m}.$$

So now we guess that $P(v_x)$ is a gaussian with variance $\sigma_x = kT/m$;

So from p 46 of these notes, we have

$$P(v_x) = \frac{1}{\sigma_x\sqrt{2\pi}}\, e^{-\frac{v_x^2}{2\sigma_x^2}}$$

$$= \frac{1}{\sqrt{\frac{kT}{m}}\sqrt{2\pi}}\, e^{-\frac{m v_x^2}{2kT}}$$

$$= \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m v_x^2}{2kT}}$$

We saw that for $kT_r \approx 4.1 \times 10^{-21}$ J, air molecules were moving at 420 m/s.

The distribution $P(\vec{v}) = P(v_x)P(v_y)P(v_z)$ is

$$P(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m\vec{v}^2}{2kT}}.$$

What is the probability distribution for speed $u = |\vec{v}|$? The volume element is

thickness of shell

$$dV = 4\pi u^2 \, du$$

area of sphere of radius u

So since $P(\vec{v})$ depends only on $\vec{v}^2$

$$P(u)\,du = P(\vec{v})\, 4\pi u^2 \, du$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mu^2}{2kT}} \, 4\pi u^2 \, du.$$

The most probable speed is the maximum of $P(u)$

$$0 = \frac{dP}{du} = \left(\frac{m}{2\pi kT}\right)^{3/2}\left(-\frac{m u^3}{kT} + 2u\right) e^{-\frac{mu^2}{2kT}} 4\pi$$

or

$$-\frac{mu^3}{kT} + 2u = 0 \qquad \text{or}$$

$$\frac{mu^2}{kT} = 2 \quad \text{or} \quad u^2 = \frac{2kT}{m} \text{ or } u = \sqrt{\frac{2kT}{m}}$$

or $u_{mp} = \sigma_x \sqrt{2}$.

The mean speed $\langle u \rangle$ is

$$\langle u \rangle = \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mu^2}{2kT}} 4\pi u^2 \; u \, du$$

$$= \frac{4\pi}{(\sigma\sqrt{2\pi})^3} \int_0^\infty du \; u \; u^2 e^{-u^2/2\sigma^2} \qquad \left(\sigma^2 = \sigma_x^2 = kT/m\right)$$

Let $y = u^2/2\sigma^2$, $\quad dy = \frac{u}{\sigma^2} du$,

$$\langle u \rangle = \frac{4\pi}{(\sigma\sqrt{2\pi})^3} \int_0^\infty \sigma^2 dy \; 2\sigma^2 y \; e^{-y}$$

$$= \frac{4\pi \, 2\sigma^4}{(\sigma\sqrt{2\pi})^3} \int_0^\infty dy \; y \; e^{-y}$$

$$0 = y e^{-y} \Big]_0^\infty = \int_0^\infty d(y e^{-y}) = \int_0^\infty dy \; e^{-y} - \int_0^\infty y e^{-y} dy \qquad \text{so}$$

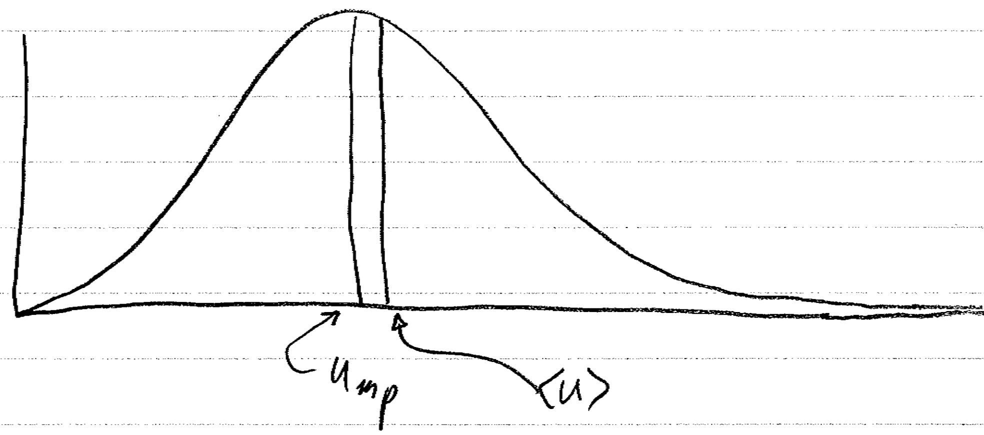
$$\int_0^\infty dy \; y \; e^{-y} = \int_0^\infty dy \; e^{-y} = -e^{-y}\Big]_0^\infty = 1.$$

So the mean speed $\langle u \rangle$ is

$$\langle u \rangle = \frac{8\pi\sigma}{2\pi\sqrt{2\pi}} = \frac{4\sigma}{\sqrt{2\pi}} \approx 1.596\,\sigma = 1.596\sqrt{\frac{kT}{m}}.$$

while the most probable $u_{mp} = \sigma\sqrt{2} \approx 1.414\,\sigma$.

The mean speed $\langle u \rangle = 1.596\,\sigma$ is slightly faster than the most probable speed $u_{mp} = 1.414\,\sigma$. Why?



Because the graph $u^2 e^{-u^2/(2\sigma^2)}$ is not symmetric about its maximum u_{mp}, the mean speed $\langle u \rangle$ can differ from the most likely speed u_{mp}. Also, $\langle u \rangle$ divides the area under the curve

$$u^2 e^{-u^2/(2\sigma^2)}$$

into two equal areas, and since the curve runs to $u \to \infty$ on the right side, it's plausible that $\langle u \rangle > u_{mp}$.

The probability that molecule 1 has $\vec{v}_1$, that molecule 2 has $\vec{v}_2$, etc., is

$$P(\vec{v}_1, \vec{v}_2, \dots \vec{v}_N)\, d^3v_1\, d^3v_2 \cdots d^3v_N$$

$$= \left(\frac{m}{2\pi kT}\right)^{\frac{3N}{2}} e^{-\frac{m\vec{v}_1^{\,2}}{2kT}}\, e^{-\frac{m\vec{v}_2^{\,2}}{2kT}} \cdots e^{-\frac{m\vec{v}_N^{\,2}}{2kT}} \times d^3v_1\, d^3v_2 \cdots d^3v_N$$

$$= \left(\frac{m}{2\pi kT}\right)^{\frac{3N}{2}} e^{-\frac{1}{2}m\left(\vec{v}_1^{\,2} + \vec{v}_2^{\,2} + \dots + \vec{v}_N^{\,2}\right)/(kT)} \times d^3v_1\, d^3v_2 \cdots d^3v_N$$

in which d^3v_i is a tiny cube in velocity space about $\vec{v}_i$.

More simply this probability distribution is

$$P(\vec{v}_1, \vec{v}_2 \dots \vec{v}_N) = \left(\frac{m}{2\pi kT}\right)^{\frac{3N}{2}} e^{-\frac{E}{kT}}$$

in which E is the total kinetic energy of the gas

$$E = \sum_{i=1}^{N} \tfrac{1}{2} m \vec{v}_i^{\,2}.$$

If the gas is in a gravitational field g, then we should include the gravitational potential energy mgz_i for each molecule at height z_i. In this case,

$$P(z_1, \vec{v}_1, z_2, \vec{v}_2, \dots z_N, \vec{v}_N) \propto e^{-\frac{E}{kT}}$$

(we suppress the normalization here)

where now the energy E

$$E = \sum_{i=1}^{N} \left(\frac{1}{2} m \vec{v}_i^{\,2} + m g z_i \right)$$

includes the gravitational energies mgz_i of all the molecules.

If we include the interactions of the molecules among themselves, then we must add the interaction energy $U(\vec{x}_1, \vec{x}_2, \dots \vec{x}_N)$

$$P(\vec{x}_1, \vec{v}_1, \vec{x}_2, \vec{v}_2, \dots \vec{x}_N, \vec{v}_N) \propto e^{-E/kT}$$

in which

$$E = \sum_{i=1}^{N} \frac{1}{2} m \vec{v}_i^{\,2} + U(\vec{x}_1, \vec{x}_2, \dots \vec{x}_N).$$

This is the Boltzmann distribution.

The probability that molecule 1 is in the tiny box of volume d^3x_1 with center $\vec{x}_1$ and has a velocity in the box d^3v_1 centered at $\vec{v}_1$, etc., is

$$d^3x_1\, d^3v_1\, d^3x_2\, d^3v_2 \cdots d^3x_N\, d^3v_N\ P(\vec{x}_1, \vec{v}_1, \vec{x}_2, \vec{v}_2 \cdots x_N v_N)$$
$$= N \exp\left(-\frac{E}{kT}\right)$$

where N is a normalization factor so that

$$1 = \int d^3x_1\, d^3v_1 \cdots d^3x_N\, d^3v_N\ P(\vec{x}_1, \vec{v}_1, \cdots \vec{x}_N, \vec{v}_N),$$

and E is the energy of all the molecules

$$E = \sum_{i=1}^{N} \tfrac{1}{2} m \vec{v}_i^{\,2} + U(\vec{x}_1, \vec{x}_2, \cdots \vec{x}_N).$$

The main contributions to $U(\vec{x}_1, \cdots \vec{x}_N)$ come from nearby pairs of molecules.

That is, most of $U(x_1, \dots x_N)$ is of the form

$$U(\vec{x}_1 \cdots \vec{x}_N) = \sum_{i<j} U(\vec{x}_i, \vec{x}_j).$$

Note that since

$$P(\text{state}) \propto \exp\left(-\frac{E(\text{state})}{kT}\right)$$

this distribution for low temperatures is highly peaked at the lowest energy state, which is called "the ground state." But at high temperatures, states of high energy occur with big probabilities.

As far as we know, these formulas are exact, when suitably interpreted. We'll derive them in chapter six.

Problem 3.2 for CO_2 & N_2

$$P_{CO_2}(z) = A\, e^{-M_{CO_2} g z/(kT)}$$

$$P_{N_2}(z) = B\, e^{-M_{N_2} g z/(kT)}$$

where $\frac{A}{B} = \frac{0.0335}{78.084} = 0.000429 \cong 4.3 \times 10^{-4}$.

$$M_{N_2} = \frac{28g}{NA} = \frac{28\ 10^{-3} kg}{6 \times 10^{23}} = 4.7 \times 10^{-26}\ kg$$

$$M_{CO_2} = \frac{12+32 g}{NA} = \frac{44\ 10^{-3} kg}{6\ 10^{23}} = 7.3 \times 10^{-26}\ kg$$

So

$$\frac{P_{CO_2}(z)}{P_{N_2}(z)} = \frac{A}{B}\, e^{-(M_{CO_2}-M_{N_2}) g z/(kT)}$$

is the ratio at height z.

With $g = 10\ m s^{-2}$ and $z = 10 km = 10^4 m$.

and $kT_r = 4.1 \times 10^{-21} J$, we have

$$\frac{P_{CO_2}(10)}{P_{N_2}(10)} = 4.3 \times 10^{-4} \exp\left(-\frac{(7.3-4.7)10^{-26} \times 10^5 J}{4.1 \times 10^{-21} J}\right)$$

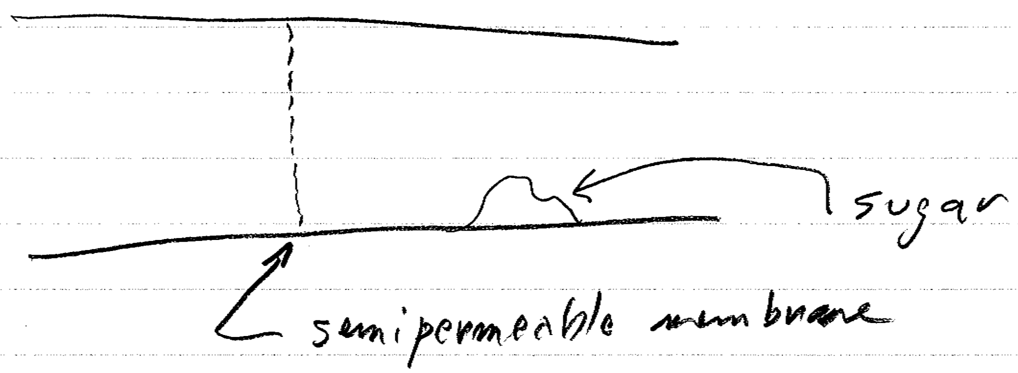
$$= 4.3 \times 10^{-4} \times e^{-2.6/4.1}$$

$$= 4.3 \times 10^{-4} \times e^{-0.634} = 4.3 \times 10^{-4} \times 0.53$$

$$= 2.28 \times 10^{-4}$$

So the carbon-dioxide level at 10 km is only 53% of what it is at sea level.

Osmotic Pressure



$$pV = NkT \quad \text{so} \quad p = \frac{N}{V}kT$$

Suppose the membrane passes water but not some other solute, for instance, sugar. Then the concentration $c_w = \frac{N_w}{V}$ will be the same on both sides of the membrane, but if we put sugar to the right of the membrane, then $c_s = \frac{N_s}{V}$ will be zero on the left and positive on the right.