

The Random Motion of Atoms: ~~Thermodynamics~~ Kinetic Theory

- How does heat lead to random motion?
- If the cell is a container for random motion how does anything useful emerge?

Probabilistic View of Large Systems:

- This room contains 10^{25} air molecules. It does not make sense to describe the motion of every molecule
- Instead, we look at average properties.
- Average/statistical properties of large #'s of particles is the subject area of Statistical Mechanics

Frequencies & probabilities: (A detour)

- Make N measurements of a quantity x :

$\Rightarrow N_1$ of x_1 ; N_2 of x_2 ; ... N_i of x_i

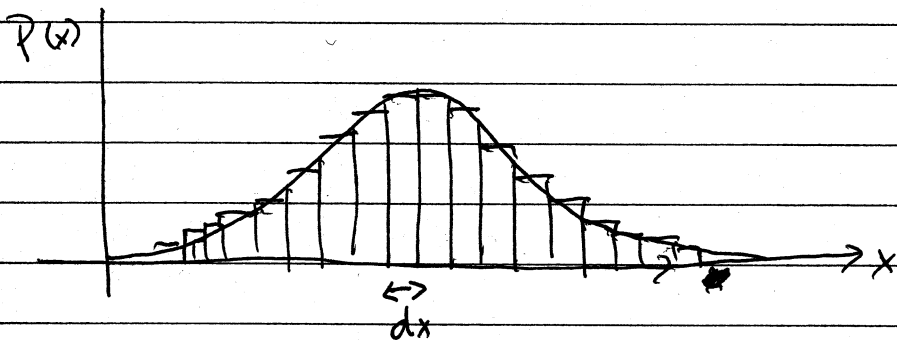
frequency of observation: $f_i = \frac{N_i}{N}$

• If you do a large # of measurements, N , then the f_i becomes the probability of observing x_i , $P(x_i)$

probabilities: $f_i = \frac{N_i}{N} \rightarrow P(x_i)$ for large N

• Normalization: $\sum_i P(x_i) = 1$

Continuous Probability distributions: What if x takes on continuous values? Make N measurements of x .



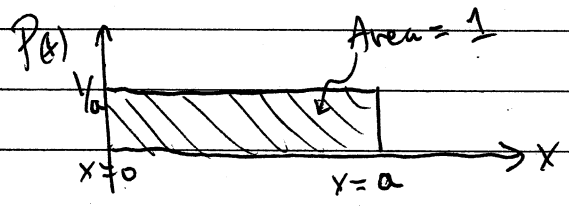
• Bin your measured x into bins of width dx

• Then $\frac{dN(x)}{N} \rightarrow P(x) dx$ for large N .

• As dx gets small the histogram will converge to the smooth curve, provided N is large.

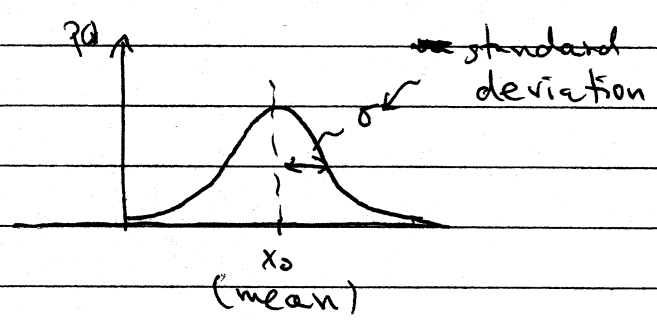
normalization: $\int dx P(x) = 1$

Uniform Distribution



$$P(x) = \begin{cases} 1/a & 0 \leq x \leq a \\ 0 & \text{otherwise} \end{cases}$$

Very important distribution: Gaussian Distribution



$$P(x) = A \exp\left(-\frac{(x-x_0)^2}{2\sigma^2}\right)$$

What is A? the distribution needs to be normalised $\int_{-\infty}^{\infty} P(x) dx = 1$

Some calculus: $\int_{-\infty}^{\infty} dz e^{-z^2} = \sqrt{\pi}$

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

let $y = \frac{(x-x_0)}{\sqrt{2}\sigma} \rightarrow dy = \frac{dx}{\sqrt{2}\sigma}$

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

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

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

- Examples of Gaussians: student grades for large classes, position of a randomly moving molecules

Mean & Variance:

Average: $\langle x \rangle = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \dots}{N}$

$$= \sum_i x_i P(x_i) \quad \text{if } N \text{ large}$$

so

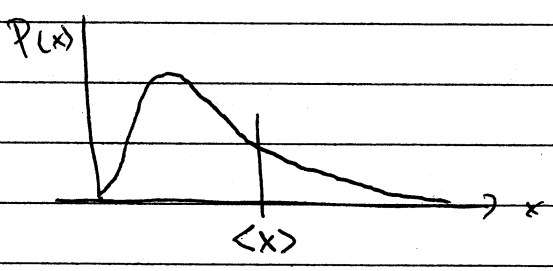
$$\langle x \rangle = \sum_i x_i P(x_i) \quad \text{discrete } x$$

or

$$\langle x \rangle = \int dx x P(x) \quad \text{continuous } x$$

for gaussian: $\langle x \rangle = x_0$

Note: $\langle x \rangle$ need not be the center or most probable value



Variance: ~~spread/error in measurement~~ spread/error in measurement

$$\sigma^2 = \sum_i (x_i - \langle x \rangle)^2 P(x_i)$$

or

$$\sigma^2 = \int dx (x - \langle x \rangle)^2 P(x)$$

e.g variance of uniform distribution:

$$\langle x \rangle = \int_0^a dx \frac{1}{a} = \frac{1}{a} \left. \frac{x}{2} \right|_0^a = \frac{a}{2} \text{ (obviously)}$$

so

$$\text{var} = \int_0^a dx (x - \langle x \rangle)^2 P(x) = \int_0^a dx (x - \frac{a}{2})^2 \frac{1}{a}$$

$$= \frac{1}{a} \int_0^a dx (x^2 - ax + \frac{a^2}{4})$$

$$= \frac{1}{a} \left[\left. \frac{x^3}{3} \right|_0^a - \left. \frac{ax^2}{2} \right|_0^a + \left. \frac{a^3}{4} \right] = \frac{1}{a} \left[\frac{a^3}{3} - \frac{a^3}{2} + \frac{a^3}{4} \right]$$

$$\text{var} = \frac{a^2}{12}$$



Probability Rules: ① prob that x_i OR x_j occur is $P(x_i) + P(x_j) \equiv$ addition rule

② prob that x_i AND y_j occur (given that they are independent) is

$$P(x_i, y_j) = P(x_i) P(y_j)$$

↑
joint prob distn

e.g: $x \equiv$ head or tail of coin & $y \equiv$ die roll

$$P(x \neq H, y = 2) = P(H) P(2) = \left(\frac{1}{2} \right) \left(\frac{1}{6} \right) = \frac{1}{12}$$

- That's it for the probability detour - it will get used later. Back to some physics & Biology.

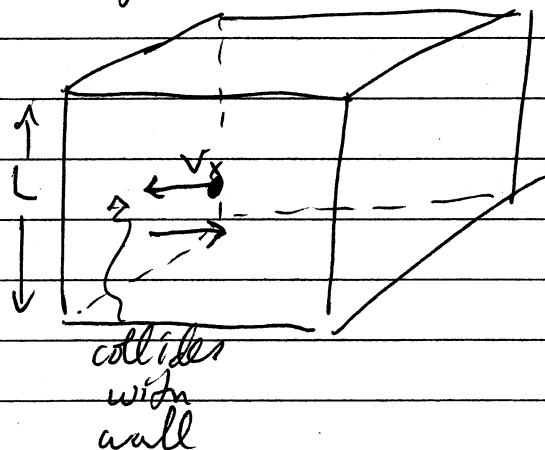
Temperature & Heat:

- Heat increases the disorder/random motion of the system.
- What about temperature? Temperature is a Statistical measure of a system's kinetic energy.
- Statistical mechanics \rightarrow understand a system's thermodynamic properties (T, P, V) in terms of microscopic properties of whole ensemble ($m, v, \&(x)$)

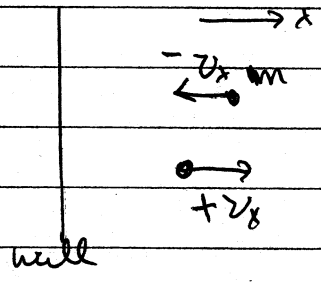
Ideal gas: $PV = N k_B T$

\uparrow total # of molecules

Let's look @ the microscopic details of an ideal gas:
Consider a large box that contains a dilute gas of N atoms each with mass m .



- The atoms are colliding with the walls of the box \equiv pressure
- What is the force exerted in one collision?



• $F_i = \frac{\Delta p_i}{\Delta t}$ \approx rate of change of momentum

Now

$$\Delta p = p_f - p_i = mv_x - (-mv_x) = 2mv_x$$

What is Δt ? Δt is time between collisions with wall \equiv time for round trip

so

$$\Delta t = 2L/v_x$$

so $F_i = \frac{\Delta p}{\Delta t} = \frac{2mv_x}{(2L/v_x)} = \frac{mv_x^2}{L}$

Total force: ~~sum of all individual forces~~

$$F_x = \sum_{i=1}^N \frac{m(v_i)_x^2}{L} = \frac{Nm}{L} \langle v_x^2 \rangle$$

\leftarrow average

• If atoms are moving randomly in each direction then $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

so $F_x = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{L}$

Pressure: $P = \frac{F}{A} = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{AL} = \frac{1}{3} \frac{Nm \langle v^2 \rangle}{V}$

\approx Volume

or

$$PV = \frac{1}{3} Nm \langle v^2 \rangle = \frac{2}{3} N \left(\frac{1}{2} m \langle v^2 \rangle \right)$$

Comparing to ideal gas law: $PV = Nk_B T$

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

avg kinetic energy

So

Temperature is a measure of the average kinetic energy of a system.

- Some #'s: O_2 molecules @ room temperature.

$$\sqrt{\langle v^2 \rangle} = v_{rms} = \sqrt{\frac{3k_B T}{m_{O_2}}}$$

$$m_{O_2} = 5.3 \times 10^{-26} \text{ kg} \quad \& \quad T = 293 \text{ K}$$

$$\Rightarrow v_{rms} = 480 \text{ m/s}$$

Distribution of velocities:

- Temperature is related to $\langle v^2 \rangle$ or the variance of the velocity distribution (~~since~~ since $\langle \vec{v} \rangle = 0$).
- What is the distribution of velocities?

• Let's talk it through:

• Consider the velocities of the gas atoms in one direction, say the x -direction.

① because they're all moving randomly, their are equal #'s moving to the left and to the right. So the average velocity in the x -direction is zero $\Rightarrow \langle v_x \rangle = 0$

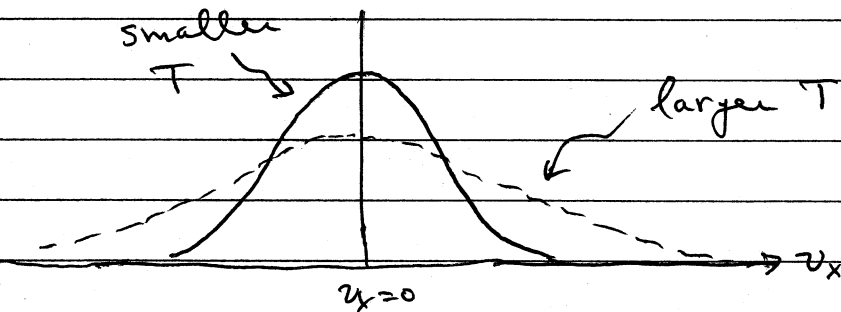
② The probability for v_x should be the same as $-v_x$, so the distribution is symmetric

③ Since $\langle v_x \rangle = 0$, then the variance $\sigma^2 = \langle v_x^2 \rangle$
or $\sigma^2 = k_B T / m$

• The Gaussian dist'n satisfies these conditions (we'll prove it later in the course)

so

$$P(v_x) \propto e^{-v_x^2 / 2\sigma^2} \quad \text{where } \sigma^2 = \frac{k_B T}{m}$$



• Thus we know the statistical behaviour of ALL the molecules in the gas with the knowledge of this distribution.

- Let's consider that we can know the position & velocity of every atom in the gas $\rightarrow (\{x_1, \vec{v}_1\}, \{x_2, \vec{v}_2\}, \dots, \{x_N, \vec{v}_N\})$
 STATE = $(\{x_1, \vec{v}_1\}, \{x_2, \vec{v}_2\}, \dots, \{x_N, \vec{v}_N\})$

- What is the probability of this state?

$$P(v_1, v_2, v_3, v_4, \dots, v_N) = P(v_1) \cdot P(v_2) \cdot P(v_3) \cdot \dots \cdot P(v_N)$$

$$\propto e^{-mv_1^2/2kT} e^{-mv_2^2/2kT} \dots e^{-mv_N^2/2kT}$$

$$= \exp\left[-\frac{1}{kT} \left(\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 + \dots + \frac{1}{2}mv_N^2\right)\right]$$

$$= \exp[-E/kT]$$

so

$$P(\text{STATE}) \propto e^{-E/kT}$$

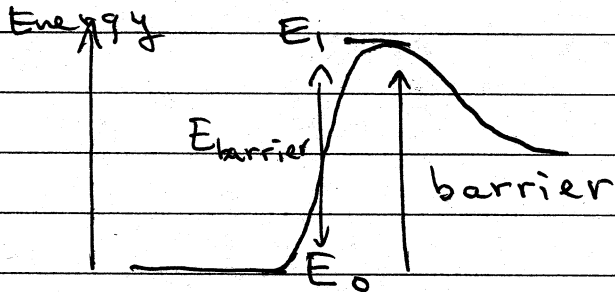
- This is the most important equation that you will learn in this course. It is the Boltzmann distribution.
- Interpretation: gives the probability of the system being a particular state. (ie. the prob of all gas molecules rushing to one corner of the room)

$$\frac{P(\text{state } i)}{P(\text{state } 0)} = e^{-(E_i - E_0)/kT} \leftarrow \text{only depends on energy difference}$$

\rightarrow gives the relative probability wrt state 0

What does all this mean?

Think about chemical reactions



- In order for reaction to take place the molecule needs to get over the energy barrier

- The probability that a molecule will have enough energy to get over the barrier, $E_{\text{barrier}} = E_1 - E_0$ is

$$P \propto e^{-\frac{E_{\text{barrier}}}{k_B T}} \equiv \text{Arrhenius Law}$$

- So ① if $E_{\text{barrier}} \gg k_B T$ the reaction will rarely occur

- ② as T increases, the reaction will become more probable

Equilibrium:

- A system left to constant external conditions will reach equilibrium, which means that the probability distributions of its physical quantities do not change.

- Friction is the conversion of mechanical energy to thermal energy in reaching equilibrium.

DNA must be a molecule:

- The inside of the cell is in thermal equilibrium.
- Many reactions are driven by thermal "kicks" (i.e. $E_{\text{barrier}} \sim kT$)
- Q: How does our genetic information get passed along without suffering mutational loss because of thermal "kicks"?
- A: DNA must be a molecule, with covalent bonds @ energies $\sim 60 k_B T$ so that random thermal collisions don't break it.
- The answer that DNA must be a chain molecule might seem obvious, but it wasn't obvious back in the 1930's before we knew what the structure of DNA was.