On the menu today

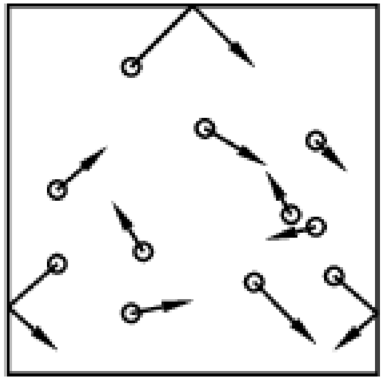
08/31/2021

Chapters 1, 2, & 3

MEETING 1

Lecture 1. *Review of basic concepts*

- In this unit we will learn about
  - What is thermodynamics?
  - Large and larger numbers
  - What is a mole?
  - The *thermodynamic limit*
  - The *ideal gas*
  - Combinatorics (combinato-what?)



Thermal physics

- Study of assemblies of large number of atoms (*macroscopic systems)*
- Why? Because thermodynamics is rooted in a *statistical* description of matter

Example:

One kilogram of nitrogen gas contains approximately 2×10^{25} N_2 molecules.

In one year, there are about 3.2×10^7 seconds, so that a 3 GHz personal computer can count molecules at a rate of roughly 10^{17} per year, if it counts one molecule every computer clock cycle.

Therefore it would take about 0.2 billion years just for this computer to count all the molecules in one kilogram of nitrogen gas (a time that is roughly a few percent of the age of the Universe!).

A mole

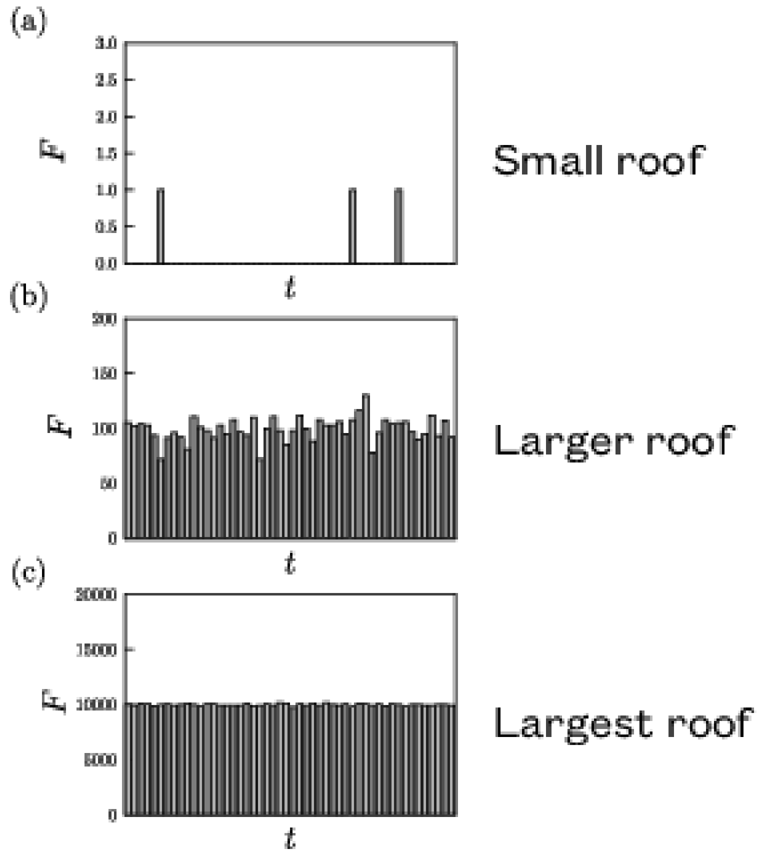
- Also about the number of atoms in 1g of $^{1}\mathrm{H}$
- That number is equivalent to **Avogadro number**
- **Molar mass** is the mass of one mole of the substance.
  - The molar mass of carbon is 12 g
  - The molar mass of water is 18 g
  - The mass of a single atom of carbon is $12/N_A$

Definitions:

1) A mole is defined as the quantity of matter that contains as many objects as the number of atoms in exactly 12 g of $^{12}\mathrm{C}$
2) $N_\mathrm{A} = 6.022 \times 10^{23}$ (Avogadro number)

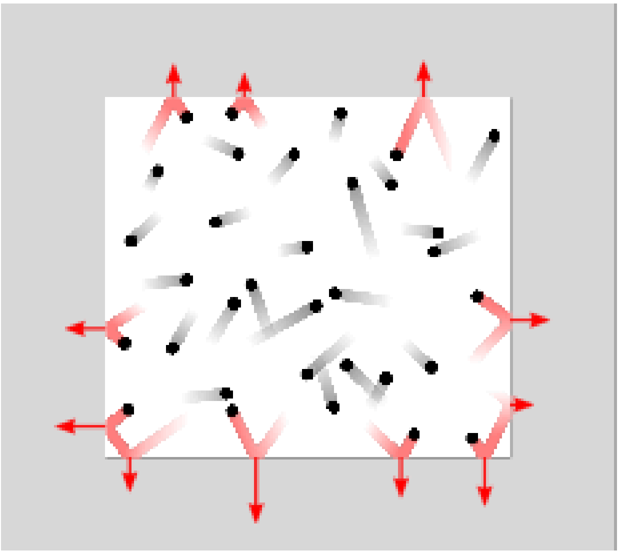
The Thermodynamic Limit

- Why can we use averages and statistics?
- **Analogy**: rain drops on a flat roof. Each drop of mass *m falls* with velocity *v* at time t, imparting an impulse $p = mv = F\Delta t$
- We now count water drops in rooms with 3 different roof sizes
  - *F* on average gets bigger for larger roofs (ok since surface area is larger)
  - Fluctuations in the force get smoothed out (do not disappear though!)
- We can normalize the result per unit of surface area: $F/A = p$, to get the pressure *p*.
- If the surface area grows to infinity, the pressure "does not" fluctuate anymore. This is called *the* ***thermodynamic limit***.



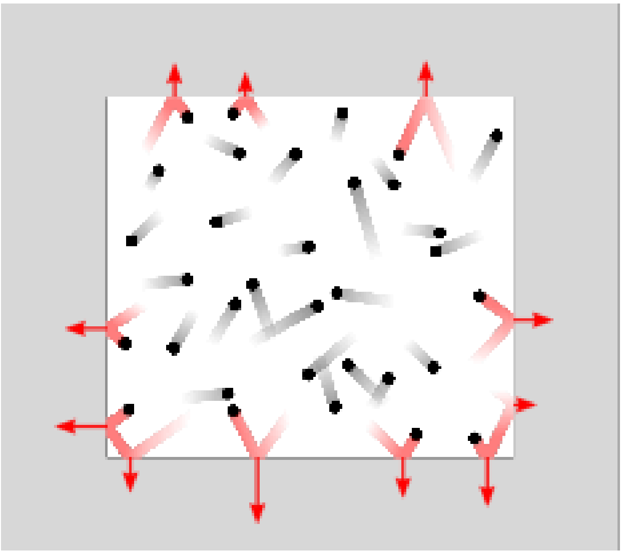
The thermodynamic limit in a gas

- Imagine a container with gas inside
- Each molecule bounces against the wall, transferring an impulse
- For a large container, the pressure is pretty much uniform in time (no fluctuations); this is because the number of molecules is extremely large
- *We describe pressure in the thermodynamic limit*



Intensive and Extensive Variables

- **Suppose container**
  - With volume V
  - At temperature T
  - At pressure p
  - Where total kinetic energy is U
- If we slice the volume in 2 (V*=V/2)
  - Total kinetic energy U*=U/2
  - p*=p and T=T*

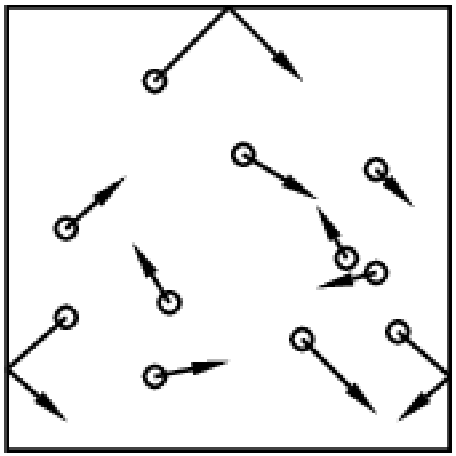


Definitions:

1) Extensive variables: those scale with the system size
2) Intensive variables: those that are independent of system size

Intensive and Extensive Variables

- **Classical Thermodynamics**
  - Macroscopic properties (e.g., p, V, T)
  - No concerns about microscopic properties (in fact: does not need it!)
- **Kinetic Theory of gases**
  - Use statistical distribution of properties of constituents
  - Individual molecules
- **Statistical Mechanics**
  - Starts from individual objects
  - Compatible with QM (properties of microscopic states)



The ideal gas

- **Experimental input:**
  - Pressure p of volume V of gas depends on its temperature T
  - Boyles' law: $p \propto 1/V$ (Boyle 1662 & Mariotte 1620)
  - Charles' law: $V \propto T$ (Charles 1787 & Gay-Lussac 1802)
  - Gay-Lussac law: $p \propto T$ (Gay-Lussac 1809)
  - Together: $pV \propto T$

$$pV = Nk_\mathrm{B}T$$

Ideal gas equation (IGE)

$pV = Nk_\mathrm{B}T$

k_B is the Boltzmann constant

Notes:

1) Purely empirical law
2) "Ideal": gas molecules do not interact; gas molecules have zero size;
3) The IGE is used profusely in thermodynamics

Combinatorial problem

○●○●○○●○●○

●●○●○●○○○○

○○●○●○○●●○

3 examples of distribution of 4 black boxes among 10

Combination

$$\Omega = \frac{n!}{(n-r)!r!} \equiv {}^{n}C_{r}$$

How many possible such configurations are there?

If we have 4 black boxes. They can be assigned to any of the 10 slots.

1. 10 possibilities for bb1
2. 9 possibilities for bb2
3. 8 possibilities for bb3
4. 7 possibilities for bb4
5. That is: 10 x 9 x 8 x 7 = 10!/(10-4)!
6. But we over-counted! Permutations among the 4 bb are equivalent.
7. Final answer: $\frac{10!}{(10-4)!4!} = 210$

Alternative proof

○●○●○○●○●○

●●○●○●○○○○

○○●○●○○●●○

3 examples of distribution of 4 black boxes among 10

How many possible such configurations are there?

4 boxes are black, 10-4 are white

1. How many ways to arrange 10 boxes? 10!
2. How many ways to arrange 4 black boxes? 4!
3. How many ways to arrange 10-6 boxes? 6!
4. Final answer: $\frac{10!}{(10-4)!4!} = 210$

Combination

$$\Omega = \frac{n!}{(n-r)!r!} \equiv {}_{n}C_{r}$$

Suppose we have 100 atoms and 40 quanta of energy to distribute among them. How many ways to do it?

$$\frac{100!}{(100-40)!40!} = 1.3710^{28}$$

Larger numbers: Stirling

Combination

$$\Omega = \frac{n!}{(n-r)!r!} \equiv {}_nC_r$$

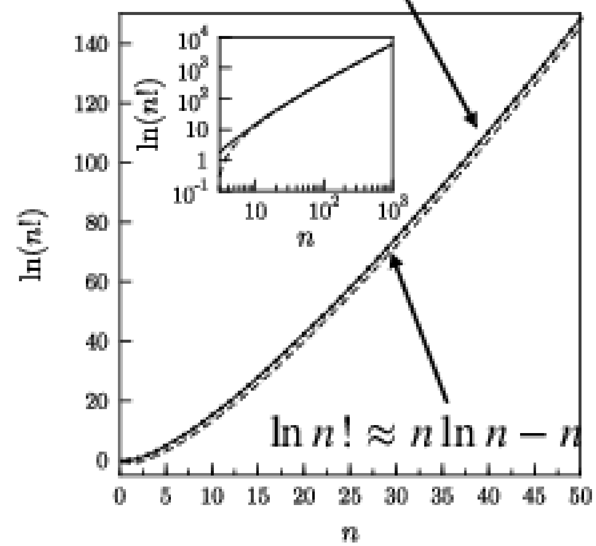
Stirling Formula

$$\ln n! \approx n \ln n - n$$

Suppose we have 100 atoms and 40 quanta of energy to distribute among them. How many ways to do it?

$$\frac{100!}{(100-40)!40!} = 1.3710^{28}$$

$$\ln n! \approx n \ln n - n + \frac{1}{2}\ln 2\pi n$$



Summary

1. The number of atoms in a typical macroscopic lump of matter is large.

   It is measured in the units of the mole. One mole of atoms contains N_{A} atoms, where $N_{\mathrm{A}} = 6.022 \times 10^{23}$

2. We introduced the concepts of intensive and extensive variables

3. We introduced the concept of thermodynamic limit

4. Combinatorial problems generate very large numbers. To make these numbers manageable, we often consider their logarithms and use Stirling's approximation: $\ln n! \approx n \ln n - n$

Test Your Knowledge

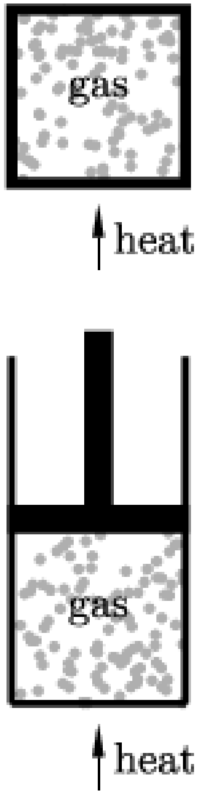
1. Among the examples listed below, which one is not an example of a system at the thermodynamic limit?
   A. Distribution of rain over a large area for a long time?
   B. water droplets falling from a leak in the roof?
   C. Clouds in the sky?
   D. The temperature of a large number of particles (N_A).
2. What is an extensive variable?
   A. a variable whose magnitude depends on the system size
   B. a variable whose magnitude does no depend on the system size
   C. It depends on the context.
3. Speaking of thermodynamic limit:
   A. it is a situation where temperature tends to zero
   B. it is a situation where fluctuations in a quantity are much smaller than the average value of that quantity
   C. It depends on the context.
4. When can we describe a system as an ideal gas when
   A. The particles do not interact attractively
   B. The particles do not interact repulsively
   C. The particles do not interact at all
   D. It depends

Lecture 2. *What is heat?*

- In this unit we will learn about
  - Definition of heat
  - Heat capacity

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$



What is heat and what is it not?

Heat is related to *energy*

Heat is related to *temperature*

Heat is related to *transfer*

} ⟶

Definition

Heat is thermal energy in transit

It is measured in Joules (J) and the rate of heating has the unit of Watts (W=J/s)

Experiment seems to indicate that:

- Heat spontaneously transfers from *hot* to *cold* bodies
  - It can transfer the other way as well *but another process must take place at the same time*
- ***In transit*** is a key attribute. An object does not possess a quantity of heat.

Heat Capacity*

- How much heat needs to be supplied to an object to raise its temperature by a small amount dT?
- **Answer**: dQ = C dT where C is the heat capacity of the object

Heat Capacity

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T}$$

*misnomer

Example

- Heat capacity of 0.125 kg of water is measured to be 523 JK^{-1} at room temperature
- What is the heat capacity of water
  - Per unit mass?: c=523/0.125=4.184 x 10^3 $JK^{-1}kg^{-1}$ (*specific* heat capacity)
  - Per unit volume?: C=4.184 x 10^3 x 1000 kgm^3=4.184 x 10^6 $JK^{-1}m^{-3}$
- **Molar heat capacity**: heat capacity of one mole of the substance

Definitions:

1) **Specific heat capacity**: HC per unit mass
2) **Molar heat capacity**: HC per mole

Exercise: calculate molar heat capacity of water

How can you heat a gas?

When we think about the heat capacity of a gas, there is a further complication.

We are trying to ask the question: how much heat should you add to raise the temperature of our gas by one kelvin?

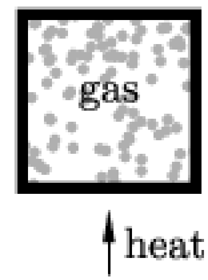
We can imagine doing the experiment in two ways.

In both cases, we are applying a constraint to the system, either constraining the volume of the gas to be fixed, or constraining the pressure of the gas to be fixed.

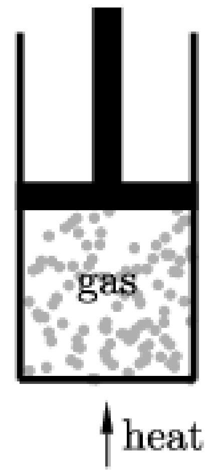
Heat Capacity…

… at constant volume: $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$

… at constant pressure: $C_p = \left(\frac{\partial Q}{\partial T}\right)_p$



Constant volume



Constant pressure

$$C_p > C_v$$

We expect that C_p will be bigger than C_V for the reason that more heat will need to be added when heating at constant pressure than when heating at constant volume.

This is because at constant pressure additional energy will be expended on doing work on the atmosphere as the gas expands.

Summary

1) Heat and heat capacity have been introduced

2) Heat is "thermal energy in transit'"

3) The heat capacity C of an object is given by $C = \mathrm{d}Q/\mathrm{d}T$.

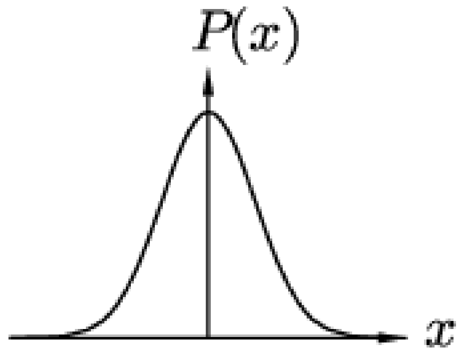
   The heat capacity of a substance can also be expressed per unit volume or per unit mass (in the latter case it is called specific heat capacity)

Test Your Knowledge

1. What is heat?
   A. A form of energy stored in a closed system
   B. A form of energy that is transferred from a hot body into a cold body
   C. A synonym of temperature
   D. None of the above
2. Is heat capacity at constant pressure larger than heat capacity at constant volume?
   A. Yes
   B. No
   C. It depends

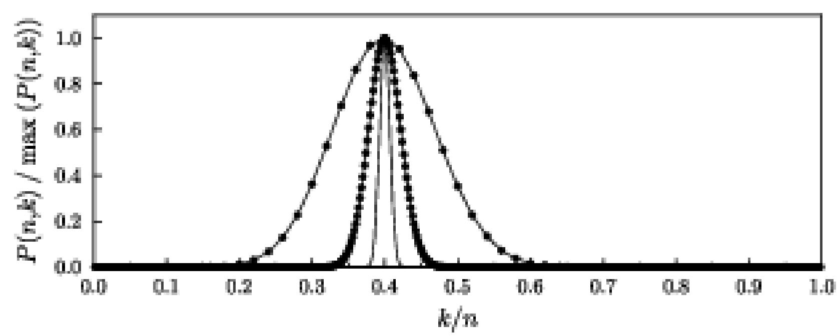
Lecture 3. *Probabilities*

- In this unit we will learn about
  - Probabilities and their impact on thermodynamics



Probability has had a huge impact on thermal physics. We are often interested in systems containing huge numbers of particles.

It follows that predictions based on probability turn out to be precise enough for most purposes.



Discrete Probability Distributions

- Let *x* be a discrete random variable which takes values x_i with probability P_i. We require that the sum of the probabilities of every possible outcome adds up to one.

$$\sum_i P_i = 1$$

- (mean, average, or expected value) is a weighting sum by the probability of each value

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

- Mean squared value of x $\langle x^2 \rangle = \sum_i x_i^2 P_i$
- In general

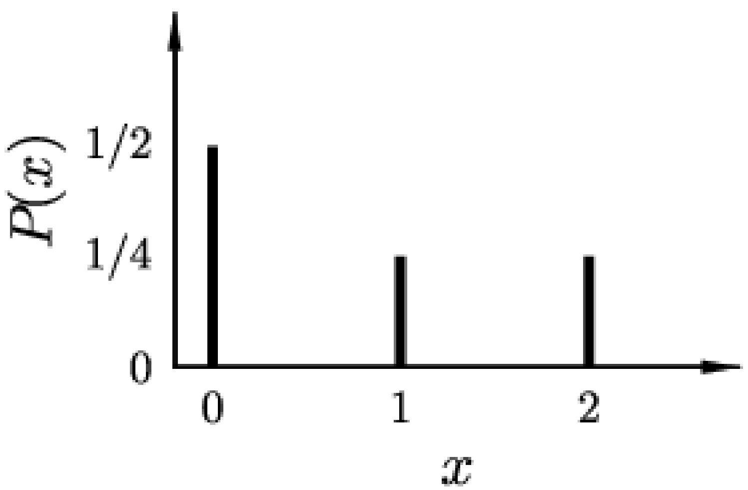
$$\langle f(x) \rangle = \sum_i f(x_i) P_i$$

Example

- Let x take values 0, 1, and 2 with probabilities 1/2, 1/4, and 1/4, respectively.

$$\begin{aligned}\langle x\rangle &= \sum_i x_i P_i \\ &= 0\cdot\frac{1}{2}+1\cdot\frac{1}{4}+2\cdot\frac{1}{4} \\ &= \frac{3}{4}.\end{aligned}$$

$$\begin{aligned}\langle x^2\rangle &= \sum_i x_i^2 P_i \\ &= 0\cdot\frac{1}{2}+1\cdot\frac{1}{4}+4\cdot\frac{1}{4} \\ &= \frac{5}{4}.\end{aligned}$$



Continuous probability distributions

- Suppose x is a continuous random variable
- It has a probability P(x) dx of having value between x and x + dx
- Total probability is 1

$$\int P(x)\,\mathrm{d}x = 1$$

- Mean value: $$\langle x\rangle = \int x\,P(x)\,\mathrm{d}x$$
- Mean of any function:

$$\langle f(x)\rangle = \int f(x)\,P(x)\,\mathrm{d}x$$

Example: Gaussian

- $<x>$ and $<x^2>$?
- Step 1: normalization

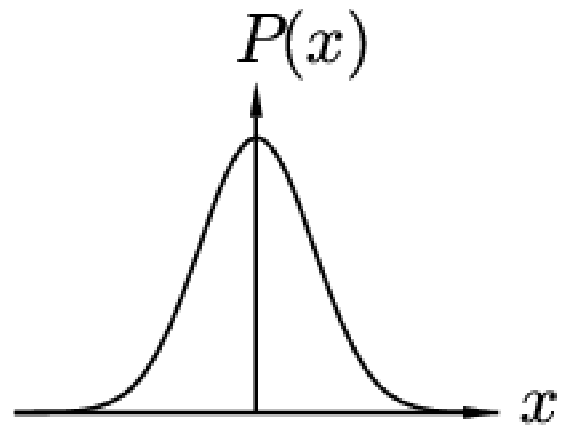
$$1 = \int_{-\infty}^{\infty} P(x)\, \mathrm{d}x = C \int_{-\infty}^{\infty} \mathrm{e}^{-x^2/2a^2}\, \mathrm{d}x = C\sqrt{2\pi a^2},$$

- Step 2: average

$$\langle x \rangle = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{\infty} x\, \mathrm{e}^{-x^2/2a^2}\, \mathrm{d}x = 0,$$

- Step 3: average of square

$$\langle x^2 \rangle = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{\infty} x^2\, \mathrm{e}^{-x^2/2a^2}\, \mathrm{d}x = \frac{1}{\sqrt{2\pi a^2}} \frac{1}{2} \sqrt{8\pi a^6} = a^2,$$



$$P(x) = C\mathrm{e}^{-x^2/2a^2}$$

Formulae

Linear transformation

- How to create a new random variable from a given one?
- Say, we have x and y $y = ax + b$
- Average $\langle y \rangle = \langle ax + b \rangle = a\langle x \rangle + b$

Variance

- How far is a variable from the mean?
  Deviation from the mean: $x - \langle x \rangle$
- How far are variables, on average, away from the mean? $\langle x - \langle x \rangle \rangle = \langle x \rangle - \langle x \rangle = 0$
- A more natural number, though mathematically tedious: $|x - \langle x \rangle|$
- To keep math happy: $(x - \langle x \rangle)^2$
- Mean squared deviation: $\sigma_x^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$
- Standard deviation is the root-mean-square

Standard deviation

$$\sigma_x = \sqrt{\left\langle (x - \langle x \rangle)^2 \right\rangle}$$

Linear transformation

- How to create a new random variable from a given one?
- Say, we have x and y $y = ax + b$
- Average $\langle y \rangle = \langle ax + b \rangle = a\langle x \rangle + b$
- Average square

$$\begin{aligned}\langle y^2 \rangle &= \langle (ax+b)^2 \rangle \\ &= \langle a^2x^2 + 2abx + b^2 \rangle \\ &= a^2\langle x^2 \rangle + 2ab\langle x \rangle + b^2\end{aligned}$$

- Standard deviation

$$\sigma_y = a\sigma_x$$

Independent variables

- If *u* and *v* are independent random variables
- The probability that u is in the range u to u+du and v is in the range v to v+dv is given by

$$P_u(u)\mathrm{d}u\, P_v(v)\mathrm{d}v.$$

The average value of the product is

$$\begin{aligned}\langle uv\rangle &= \iint uvP_u(u)P_v(v)\,\mathrm{d}u\,\mathrm{d}v\\ &= \int uP_u(u)\,\mathrm{d}u\int vP_v(v)\,\mathrm{d}v\\ &= \langle u\rangle\langle v\rangle,\end{aligned}$$

- The separation of variables is possible because they are independent

Two random variables are independent if knowing the value of one of them yields no information about the value of the other.

For example, the quality of your favorite soccer team and the number of days you may stay in confinement due to covid-19.

n random variables

- Suppose you have n random variable with same mean and variance σ_X^2
- If $Y=X_1+X_2+X_3+\ldots X_n$
- The mean $\langle Y\rangle=\langle X_1\rangle+\langle X_2\rangle+\langle X_3\rangle+\ldots\langle X_n\rangle= n\langle X\rangle$
- Variance of Y?

$$\begin{aligned}\langle Y^2\rangle &= \langle X_1^2+\cdots+X_N^2+X_1X_2+X_2X_1+X_1X_3+\cdots\rangle \\ &= \langle X_1^2\rangle+\cdots+\langle X_N^2\rangle+\langle X_1X_2\rangle+\langle X_2X_1\rangle+\langle X_1X_3\rangle+\cdots\end{aligned}$$

n terms like $\langle X^2\rangle$

n(n-1) terms line $\langle X_1X_2\rangle \to \langle X_1\rangle\langle X_2\rangle=\langle X\rangle^2$

$$\langle Y^2\rangle = n\langle X^2\rangle + n(n-1)\langle X\rangle^2$$

$$\begin{aligned}\sigma_Y^2 &= \langle Y^2\rangle-\langle Y\rangle^2 \\ &= n\langle X^2\rangle - n\langle X\rangle^2 \\ &= n\sigma_X^2.\end{aligned}$$

Consequence: measurements

$$\sigma_Y^2 = n\sigma_X^2$$

Imagine that a quantity X is measured n times, each time with an independent error, which we call σ_X.

If you add up the results of the measurements to make $Y = \sum X_i$, then the rms error in Y is only $\sqrt{n}$ times the rms error of a single X. Hence if you try and get a good estimate of X by calculating $\left(\sum X_i\right)/n$, the error in this quantity is equal to $\sigma_X/\sqrt{n}$

Consequence: random walk

Imagine a drunken person staggering out of a pub and attempting to walk along a narrow street (which confines him or her to motion in one dimension).

Suppose the drunken person is equally likely to travel one step forwards or one step backwards. The effects of intoxication are such that each step is uncorrelated with the previous one.

- Thus the average distance travelled in a single step is $\langle X \rangle = 0$
- After n such steps, we would have an expected total distance travelled of $\langle Y \rangle = \sum \langle X_i \rangle = 0$
- However, in this case the root mean squared distance is more revealing. In this case $\langle Y^2 \rangle = n \langle X^2 \rangle$
- It follows that the rms length of a random walk of n steps is $\sqrt{n}$ times the length of a single step.

Binomial distribution

Bernoulli Trial

- Two possible outcomes
- One with probability p ("success")
- One with probability 1-p ("failure")

$$\begin{aligned} \langle x \rangle &= 0 \times (1-p) + 1 \times p = p \\ \langle x^2 \rangle &= 0^2 \times (1-p) + 1^2 \times p = p \\ \sigma_x &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{p(1-p)} \end{aligned}$$

Binomial distribution

Binomial distribution

The binomial distribution is the discrete probability distribution $P(n,k)$ of getting k successes from n independent Bernoulli trials.

What is $P(n,k)$?

(1) probability of $p^k(1-p)^{n-k}$ (*k successes and n-k failures)*

(2) *How many possibilities?* ${}^nC_k$

$$P(n,k) = {}^nC_k p^k (1-p)^{n-k}$$

Algebra

$$P(n,k) = {}^{n}C_k p^k (1-p)^{n-k}$$

$$(x+y)^n = \sum_{k=0}^{n} {}^{n}C_k \, x^k y^{n-k}$$

Mean, variance, etc

The binomial distribution is just the sum of *independent* Bernoulli trials.

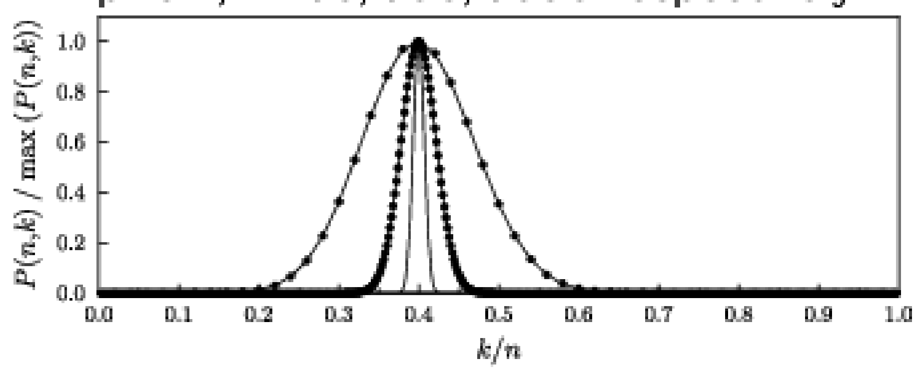
Therefore: $$\langle k \rangle = np$$

Also: $$\sigma_k^2 = np(1-p)$$

The fractional width is: $\sigma_k/\langle k \rangle = \sqrt{(1-p)/np}$

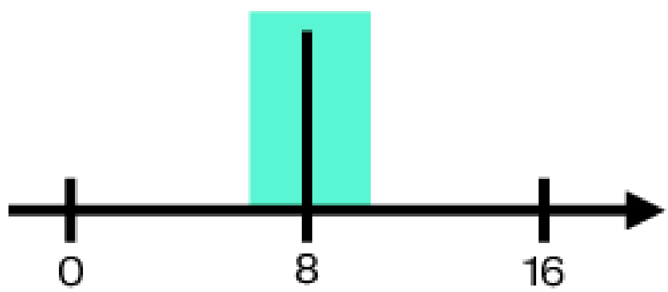
This decreases as n increases!

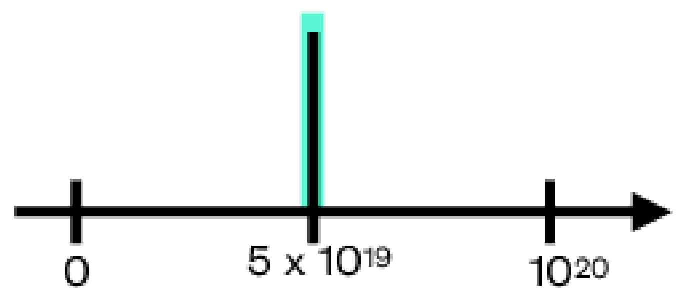
p=0.4; n= 50, 500, 5000 respectively



Example 1: fair coin

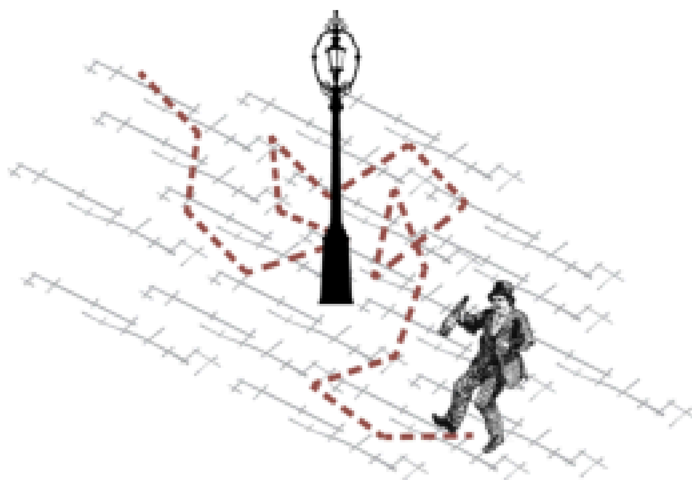
- p=0.5
- n=16 -> the expected number of heads <h>=np=8; with standard deviation of 2
- For n=10^{20} -> the expected number of heads is <h>=5 x 10^{19}, with standard deviation of 5 x 10^{9}. The standard deviation is, in relative terms, much smaller





Example 2: random walk (1D)

- Equivalent to n Bernoulli trials ($+L$ forwards or $-L$ backwards with equal probability $p = 0.5$. If we have n steps, k of them forwards, the distance travelled is:
  $x = k \times (+L) + (n - k) \times (-L) = (2k - n) \times L$
- Mean distance $\langle x \rangle = 2 < k > \times L = 0$
- Standard deviation $\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{n}L$



Test Your Knowledge

1. How many ways can you pick 5 objects from a collection of 9?
   - A. 126
   - B. 128
   - C. 63
   - D. 54
2. Imagine a random walk in one dimension (problem often called *the drunken salesman*). We will suppose that each step size to be equal to 1). What is the most accurate statement below?
   - A. After n steps, the drunken salesman will, on average, end up at a distance $d = n$.
   - B. After n steps, the drunken salesman may have been found, at some point, at a distance of about $\sqrt{n}$ away from his starting point, for a large enough value of n .
   - C. After n steps, the pedometer on the wrist of the drunken salesman will measure exactly $n/2$ steps by the time he reaches the end of the street.
   - D. None of the other answers is correct.
3. What is a Bernoulli trial?
   - A. It is an event when Bernoulli went to jail because he stole a plane.
   - B. It is an experiment with only two possible outcomes
   - C. It is the event when the definition of temperature was finalized