Probability

Flipping a coin

		probability
two outcomes	H	$1/2$
	T	$1/2$

postulate of equal a priori probabilities

probability gives relative likelihood of possible outcomes. UNITLESS

Flipping two coins

H H	4 outcomes
H T	distinguishability!!
T H	microstates
T T	

Define $P(i)$ to be probability of getting i heads

i is a random variable

$$
\left.\begin{aligned}
P(0) &\propto 1 \\
P(1) &\propto 2 \\
P(2) &\propto 1 \\
P(i>2) &= 0
\end{aligned}\right.
$$

$P(1) \propto 2$ — $\left\{ \begin{matrix} TH \\ HT \end{matrix} \right.$ degenerate outcomes

Normalize P s.t. $\sum \text{prob} = 1$

$$\tilde{P}(i) = P(i) / \sum_i P(i)$$

normalization factor

We are always free to normalize.

For discrete events

$$\tilde{P}(i) = \frac{\text{degeneracy of } i}{\text{total events/outcomes}}$$

Coin toss example of binomial trial

n tosses $\longrightarrow$ 2^n possible outcomes

i heads out of n $\longrightarrow$ ${}_nC_i$ or $\binom{n}{i}$

$$\frac{n!}{i!(n-i)!}$$

(# of ways to arrange n coins)

(# of ways to arrang i heads + $n-i$ tails)

$$\tilde{p}(i) = \frac{{}_nC_i}{2^n}$$

What happens to $\tilde{P}(i)$ as $n \to \infty$?

Example of discrete probabilities

50 students in class, HW defense is 5 random students, what are your odds of being in that 1st group?

How many groups of 5? $\binom{50}{5} = 2118760$

How many groups contain you?

$$\binom{49}{4} = 211876$$

$P(\text{you}) = 1/10$ (obvious, 1/10 chance each week!!)

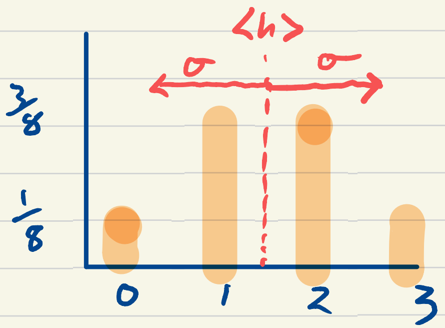
Probability all sophomores?

Back to coins

$n = 3 \qquad 2^3 = 8$

h

$\binom{3}{0} = \binom{3}{3} = 1 \qquad \binom{3}{1} = \binom{3}{2} = 3$



most probable? $\qquad \tilde{P}(1) = \tilde{P}(2) = 3/8$

expected value?

$$\langle h \rangle \equiv \sum_h h \tilde{P}(h) = 0 \cdot \frac{1}{8} + 1 \cdot \frac{3}{8} + 2 \cdot \frac{3}{8} + 3 \cdot \frac{1}{8}$$

$$= 3/2$$ not a possible value!

Can find expected value of any fn of h

$$\langle f(h) \rangle = \sum_h f(h) \tilde{P}(h) = \sum_h f(h) P(h) \Big/ \sum_h P(h)$$

mean $= \langle x \rangle$

mean squared $= \langle x^2 \rangle$

rms $= \langle x^2 \rangle^{1/2}$

variance $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

std deviation $\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

Gives "width of distribution

3 Coins example

$$\langle h^2 \rangle = 0^2 \cdot \frac{1}{8} + 1^2 \cdot \frac{3}{8} + 2^2 \cdot \frac{3}{8} + 3^2 \cdot \frac{1}{8}$$

$$= \frac{3}{8} + \frac{12}{8} + \frac{9}{8} = 3$$

$$\langle h^2 \rangle^{1/2} = \sqrt{3} \neq \langle h \rangle \;!!$$

$$\sigma^2 = \langle i^2 \rangle - \langle i \rangle^2$$

$$= 3 - \left(\frac{3}{2}\right)^2 = 3/4$$

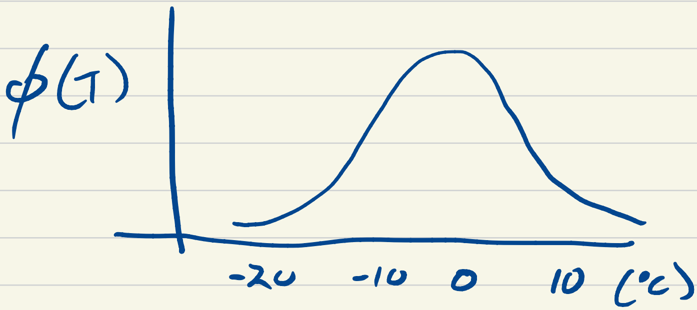
$$\sigma = \sqrt{3}/2$$

Interesting to think about how $\langle h \rangle$ & σ_h grow with N...

Continuous probability densities

High T in S.B. in January

Could collect data, any real # possible



$\phi(T)$ has units 1/°C   probability density

Probability of $T = 0.000°C \rightarrow 0$!!

Evaluate ranges

$$P(-10 < T < 0) \propto \int_{-10}^{0} \phi(T)\, dT$$

unitless

$$P(T > 10) \propto \int_{10}^{\infty} \phi(T)\, dT$$

Can normalize $\tilde{\phi}(T) = \dfrac{\phi(T)}{\int_{-273}^{\infty} \phi(T)\, dT}$

Example

$$\phi(T) = e^{-(T-20)^2/50}$$

see python notebook

Boltzmann probability central probability dist of physical chem. Discovered by Ludwig Boltzmann in 1800's.

Determines probability of an object to have an energy E, parametric in temperature T.

always a ftn of some internal variables

$$P(E) \propto e^{-E(\underline{q},p)/k_B T}$$

$k_B = 1.3807 \times 10^{-23}$ J/K Boltzmann's const.

energy? fundamental physical quantity
comes in many forms
kinetic, potential, light
ftn of internal DOFs $E(\underline{q},p)$
Conserved in a closed system

energy units
SI : J : $kg\frac{m^2}{s^2}$ $\rightleftarrows$ kJ/mol

$eV = 1.6 \times 10^{-19}$ J $= 96.5$ kJ/mol

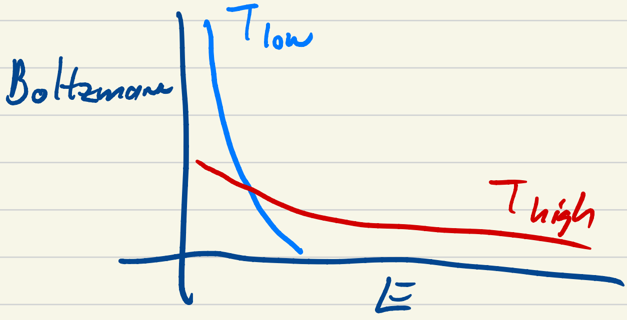
temperature units

absolute T, Kelvin

"Temperature" is a characteristic of a system that follows Boltzmann statistics. Characteristic of all large systems @ equilibrium.

Sets an energy scale

T	$k_B T$
0	0
298 K	0.026 eV = 2.5 kJ/mol
1000 K	0.086 eV = 8.3 kJ/mol



(often reflect plot)

Ex: gases in atmosphere

gravitational potential energy:

$$\varepsilon(h) = mgh$$

Probability density to be at height h at temperature T?

$$\phi(h) \propto e^{-mgh/kT}$$

Normalize:

$$\int_0^\infty \phi(h)\,dh = k_B T/mg$$

$$\tilde{\phi}(h) = \frac{mg}{kT} e^{-mgh/kT}$$

Table 2: car vs gas molecule

	car	molecule
m	~ 1000 kg	$\sim 10^{-26}$ kg
mgh	9800 J 6.1×10^{22} eV	9.8×10^{-26} J 6.1×10^{-7} eV
kT @ 298K	0.026 eV	
mgh/kT	2.4×10^{24}	2.3×10^{-5}
$\tilde{\phi}(1m)/\tilde{\phi}(0m)$	0	0.99998
$\langle h\rangle$	0	42 km !!

Size matters!!

Basis of barometric law that pressure decays ~ exponentially w/ altitude. (right only if isothermal!!)

$$Pres(h_0) = \frac{N(h>h_0)\cdot m\cdot g}{Area} \Longrightarrow$$

$$Pressure / Press(0) = e^{-mgh/kT}$$

Does atmosphere go forever? No... gas molecules can exceed escape velocity and leak out. No He or H_2 in atmosphere!!

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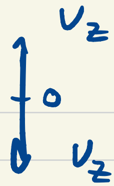
equipartion - Boltzmann applies to kinetic + potential energies each alone

Ex : kinetic energy



$$-\infty < v_z < \infty$$

$$\varepsilon_{kin}(v_z) = \frac{1}{2} m v_z^2$$

$$\phi(v_z) \propto e^{-\frac{1}{2} m v_z^2 / kT}$$

normalize

$$\int_{-\infty}^{\infty} \phi \, dv = \left(\frac{2\pi kT}{m}\right)^{1/2}$$

$$\tilde{\phi}(v_z) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-m v_z^2 / 2kT}$$

Bell shaped curve → "Gaussian"

$$G(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$$

by inspection

$$\langle v_z \rangle = \mu = 0$$

$$\langle v_z^2 \rangle = \sigma^2 = k_B T / m$$

See Figure 2

	car	molecule
m	1000 kg	10^{-26} kg
$\left(\frac{kT}{m}\right)^{1/2}$ @298K	2×10^{-12} m/s	640 m/s (!)

rms velocity

Expectation values

"average" value of a random variable

ex 2 coins

$$\langle i \rangle = \bar{i} = \tfrac{1}{4}\cdot 0 + \tfrac{1}{2}\cdot 1 + \tfrac{1}{4}\cdot 2 = 1$$

Generally $\langle i \rangle = \sum_i i \tilde{P}(i)$

$$= \sum_i i P(i) \Big/ \sum_i P(i)$$

Can evaluate for functions of i

$$\langle i^2 \rangle = \sum_i i^2 \tilde{P}(i) = 3/2$$

$$\langle i \rangle^2 \neq \langle i^2 \rangle \quad !!$$

Generally $\langle f(i) \rangle = \sum_i \tilde{P}(i) \cdot f(i)$

-or- $\int \tilde{\phi}(x) \cdot f(x) dx$

mean $= \langle x \rangle$

mean squared $= \langle x^2 \rangle$

rms $= \langle x^2 \rangle^{1/2}$

most probable ?

variance $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

std deviation $\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

Gives "width of distribution

2 Coins example

$$\sigma^2 = \langle i^2 \rangle - \langle i \rangle^2$$

$$= \tfrac{3}{2} - 1 = \tfrac{1}{2}$$

T distribution example

$$\phi(T) = e^{-(T-20)^2/50}$$

see python notebook