The Boltzmann Distribution

Physics/Neuro 141

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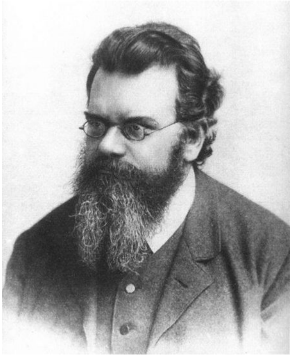
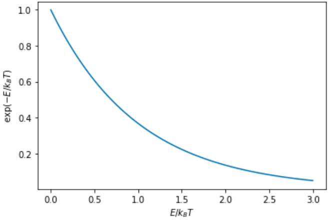
Week 1



AN ENERGY DISTRIBUTION AT THERMAL EQUILIBRIUM



- Thermal energy is exponentially distributed by the Boltzmann equation: $P(E) \propto e^{-\frac{E}{k_B T}}$
- When large numbers of systems interact and freely exchange energy, the energy of any given system upon any given observation follows an exponential distribution.

Discrete energy levels (ϵ_1, ϵ_2, ... ϵ_M)

Normalized probability distribution

$$p_i = \frac{1}{Q} e^{-\epsilon_i/kT} = \frac{e^{-\epsilon_i/kT}}{\sum_{j=1}^{M} e^{-\epsilon_j/kT}}$$

Relative probability of two states

$$\frac{p_i}{p_j} = e^{\frac{\epsilon_j - \epsilon_i}{kT}}$$

A "Boltzmann" understanding of the exponential atmosphere

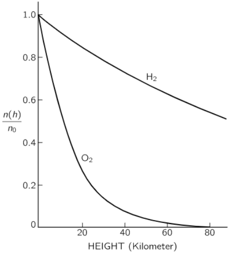


Fig. 40–2. The normalized density as a function of height in the earth's gravitational field for oxygen and for hydrogen, at constant temperature.

Air density is a function of potential energy

$$\rho(h) \propto e^{\frac{-mgh}{k_B T}}$$

A "Boltzmann" understanding of chemical reactions

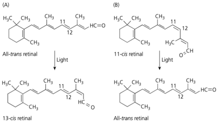
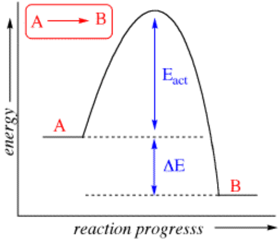


Figure 9.1 Retinal chromophores of visual pigments: photoisomerization. (A) In archaeobacteria, all-*trans* retinal is isomerized by light to 13-*cis* retinal. (B) In most animals, the chromophore is 11-*cis* retinal, which is isomerized by light to the all-*trans* form.



Relative likelihood of two states

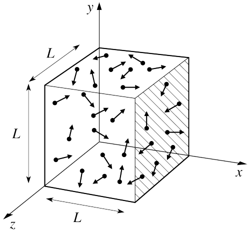
$$\frac{p_A}{p_B} = e^{-\frac{\Delta E}{k_B T}}$$

Forward rate

$$k_{A \Rightarrow B} \propto e^{-\frac{E_{act}}{k_B T}}$$

Counting Method to derive the Boltzmann distribution

N weakly interacting systems divide total E energy among them



Fundamental question

How many, n_s, of the N systems do we expect to be in the state s that is associated with energy ϵ_s?

average energy of the system

$\overline{\epsilon} = \frac{\sum_s n_s \epsilon_s}{\sum_s n_s}$

probability of being in state s

$f_s = n_s / N$

average energy

$\sum_s f_s \epsilon_s = \overline{\epsilon}$

$\sum_s f_s = 1$

State	Energy	Number
1	ϵ_1	n_1
2	ϵ_2	n_2
3	ϵ_3	n_3
.	.	.
.	.	.
s	ϵ_s	n_s
.	.	.
.	.	.

Conservation of mass and energy

$\sum_s n_s = N$

$\sum_s n_s \epsilon_s = U$

What is the probability of a particular distribution of n_s?

$W = \frac{N!}{n_1!n_2!n_3!\ldots}$
the number of ways you can have a specific number of particles at each energy level

Find the distribution with the largest number of possibilities, i.e., maximize W

Maximize $\log W$

$$
\begin{aligned}
\log W &= \log N! - \sum_s n_s! \\
&= N(\log N - 1) - \sum_s n_s(\log n_s - 1)
\end{aligned}
$$

Stirling's formula

$N! = \left(\frac{N}{e}\right)^N$

Maximize W with constraints of conservation of mass and energy

Lagrange multipliers

Add N and U to $\log W$, each multiplied by an arbitrary Lagrange multiplier (α and β).

The most probable W is that for which:

$$\delta\left(\log W - \alpha \sum_s n_s - \beta \sum_s \epsilon_s n_s\right) = 0$$

Varying with respect to each n_s gives:

$$-\sum_s \delta n_s \left(\log n_s + \alpha - \beta \epsilon_s\right) = 0$$

The Boltzmann distribution

$$\overline{n_s} = e^{-\alpha} e^{-\beta \epsilon_s}$$

Using information theory to derive the Boltzmann distribution

The entropy $H(X)$ of a random variable X

$$H(X) = -\sum_{x \in X} p(x) \log_2 p(x)$$

$$H(X) = \langle \log_2 p(x) \rangle$$

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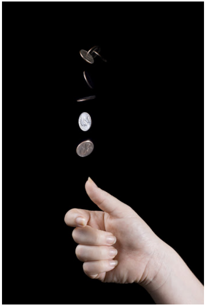
The entropy of a coin toss



```
In [1]: import numpy as np
        import matplotlib.pyplot as plt
```

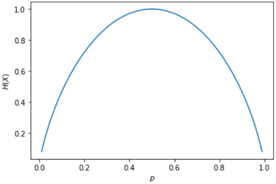
```
In [7]:     p = np.linspace(0, 1, 100)
            H = -p*np.log2(p)-(1-p)*np.log2(1-p)

            plt.figure()
            plt.plot(p, H)
            plt.xlabel('$p$')
            plt.ylabel('$H(X)$')

            plt.show()
```

```
/Users/aravinthansamuel/anaconda3/lib/python3.7/site-package
s/ipykernel_launcher.py:2: RuntimeWarning: divide by zero en
countered in log2

/Users/aravinthansamuel/anaconda3/lib/python3.7/site-package
s/ipykernel_launcher.py:2: RuntimeWarning: invalid value enc
ountered in multiply
```



Maximum entropy distribution with fixed mean

- Maximize entropy :

$$H(p) = -\sum_{i=1}^{N} p_i \log p_i$$

- Normalization condition:

$$\sum_{i=1}^{N} p_i = 1$$

- Fixed mean:

$$\sum_{i=1}^{N} p_i \epsilon_i = E$$

Use Lagrange multipliers:

$p_i \propto e^{-\lambda \epsilon_i}$

An exponential distribution of energies is the distribution with the least bias.