Part II : Models of statistical physics

Topics of Part II:

- ("Foundations" of) statistical physics, Boltzmann distribution
- Ising model
- Mean field Ising model
- Self-avoiding polymer

Today

- (information theoretic) entropy
- Boltzmann distribution
- temperature, free energy...
- ideal gas, Maxwell-Boltzmann distribution

Section 1 Boltzmann distribution

History

- Daniel Bernoulli (1700-1782), kinetic theory of gases (temperature, pressure)
- James ~~Clerk~~ Maxwell (1831-1879)
  Ludwig Boltzmann (1844-1906)
  $\rightsquigarrow$ Maxwell-Boltzmann distribution
- J. Willard Gibbs (1839-1903)
  "Father of stat. phys" E.g. statistical ensembles.

Entropy

Let $\Omega = \{x_1, \dots, x_n\}$ be finite prob. space and $\mathbb{P}$ prob. meas. on Ω. $p_k = \mathbb{P}[x_k]$

Definition Entropy of $\mathbb{P}$ is defined as

$$S(\mathbb{P}) = K \sum_{k=1}^{n} -p_k \log p_k$$

where K is a constant that we choose to be $K=1$ usually.

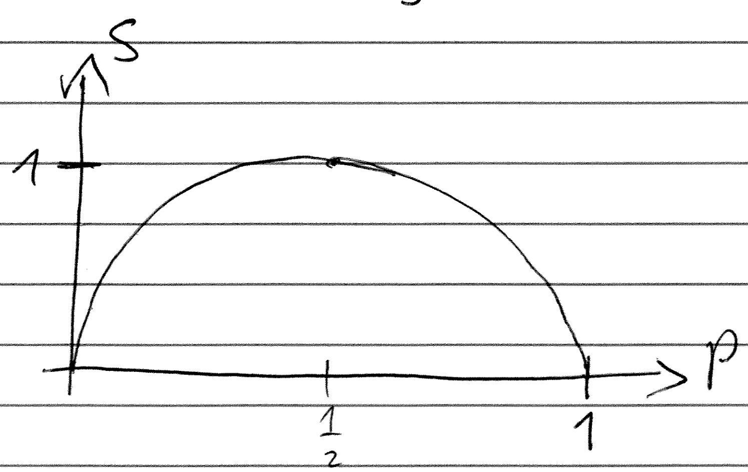
Remark In thermodynamics K is Boltzmann constant and its unit is JK^{-1} (Joule per Kelvin). In information theory $K = (\log 2)^{-1}$ and the unit is bit.

Example (Entropy of biased coin)

$X \sim \text{Bernoulli}(p) \Leftrightarrow \mathbb{P}[X=1]=p, \mathbb{P}[X=0]=1-p$

Entropy in bits:

$$S(\mathbb{P}) = \frac{-p\log p - (1-p)\log(1-p)}{\log 2}$$



Example (Entropy of unif. distribution)
If $\mathbb{P}$ is uniform, $\mathbb{P}[x_k] = \frac{1}{\#\Omega}$, then

$$S(\mathbb{P}) = \log \#\Omega$$

This is Boltzmann's formula for entropy.
(E.g. in very large system distribution is almost unif. distributed on $E = \text{const.}$ surface.)

Entropy measures disorder: it is positive, additive and maximized at equilibrium (we will come back to this in some systems with dynamics). Now we'll study probability measures that maximize entropy.

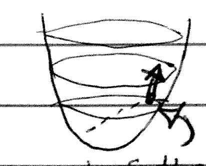
Example (Maximizing entropy)
Let's solve the following convex optimization problem with an equality constraint:

$$\begin{cases} \min \sum_k p_k \log p_k \\ \text{subject to } \sum_k p_k = 1 \\ \quad (p_k \geq 0 \ \forall k) \end{cases}$$

Lagrange multiplier $\lambda \in \mathbb{R}$. The gradient of

$$\sum_k p_k \log p_k + \lambda \left(\sum_k p_k - 1 \right)$$

has to vanish.



normal of the surface $\sum_k p_k = 1$ is parallel to grad of $\sum_k p_k \log p_k$

$$\Rightarrow \log p_k + 1 + \lambda = 0 \quad \forall k$$

$$\Rightarrow p_k = \frac{1}{\#\Omega}, \quad \lambda = (\log \#\Omega) - 1$$

Boltzmann distribution

Example (Boltzmann distribution from maximum entropy principle)

Suppose that $\phi : \Omega \to \mathbb{R}$ is a random variable and we have measured $\mathbb{E}_{\mathbb{P}}[\phi] = F_0$.
What is the "most disordered" $\mathbb{P}$ given the constraint?
Optimize:

$$\begin{cases} \min \sum_{k=1}^{n} p_k \log p_k \\ \text{subject to} \quad \sum_{k=1}^{n} p_k = 1 \\ \sum_{k=1}^{n} p_k \phi(x_k) = F_0 \\ (p_k \geq 0) \end{cases}$$

Lagrange multipliers $\lambda, \beta \in \mathbb{R}$. The gradient ($\nabla_p$) of the following expression has to vanish

$$\sum_{k=1}^{n} p_k \log p_k + \lambda\left(\sum_{k=1}^{n} p_k - 1\right) + \beta\left(\sum_{k=1}^{n} p_k \phi(x_k) - F_0\right)$$

$$\Rightarrow \log p_k + \lambda + 1 + \beta\phi(x_k) = 0 \quad \forall k$$

$$\Rightarrow \begin{cases} p_k = \frac{1}{Z(\beta)} \exp(-\beta\phi(x_k)) \\ [\lambda = \log Z(\beta) - 1] \end{cases}$$

Here $Z(\beta) = \sum_{k=1}^{n} \exp(-\beta\phi(x_k))$. Solve β from

$$F_0 = \mathbb{E}_\beta[\phi] = \frac{\sum_{k=1}^{n} \phi(x_k)\exp(-\beta\phi(x_k))}{Z(\beta)} = -\partial_\beta \log Z(\beta)$$

Notice that

$$\partial_\beta\left(-\partial_\beta \log Z(\beta)\right) = -\left[\frac{\partial_\beta^2 Z}{Z} - \left(\frac{\partial_\beta Z}{Z}\right)^2\right]$$
$$= -\mathbb{E}_\beta\left[\left(\phi - \mathbb{E}_\beta[\phi]\right)^2\right] \leq 0$$

So $\mathbb{E}_\beta[\phi]$ is decreasing function of β and the solution to $\mathbb{E}_\beta[\phi] = F_0$ is unique.

<u>Definition</u> (Boltzmann distribution)
Let Ω be a finite set of states and $H : \Omega \to \mathbb{R}$ a function which we call <u>energy</u> or <u>Hamiltonian</u> of the system. Let $\beta \geq 0$ define the <u>partition function</u> (German Zustandssumme)

$$Z(\beta) = \sum_{x \in \Omega} \exp(-\beta H(x))$$

and the <u>Boltzmann distribution</u> (Gibbs distr.)

$$\mathbb{P}_\beta(x) = \frac{1}{Z(\beta)} \exp(-\beta H(x))$$

<u>Remark</u> $\beta = 0$ uniform distribution $(T = \infty)$

$\beta \to \infty$: if x^* s.t. $H(x^*) < H(x)$ $\forall x \neq x^*$, then

$$\mathbb{P}_\infty[x] = \delta_{x,x^*}$$ minimum energy configuration $(T = 0)$

$\beta \mapsto \mathbb{E}_\beta[H]$ is decreasing.

$\beta(T)$ should be decreasing.
↑ temperature

Equilibrium of two systems

Suppose that we are given two systems $\Omega_1 = \{x \in \Omega_1\}$, $\Omega_2 = \{y \in \Omega_2\}$.
In beginning they have their own Boltzmann distributions. Then

$$\mathbb{P}_{\beta_1,\beta_2}[x,y] = \frac{\exp(-\beta_1 H_1(x) - \beta_2 H_2(y))}{Z_1(\beta_1) Z_2(\beta_2)}$$

Suppose that they interact very weakly so that the total Hamiltonian is still $H_1 + H_2$, but they can exchange energy. By maximum entropy principle in the end (in equilibrium), the distribution is

$$\mathbb{P}_{\beta_{12}}[x,y] = \frac{\exp(-\beta_{12}(H(x)+H(y)))}{Z_{12}(\beta_{12})}$$

where β_{12} satisfies

$$\mathbb{E}_{\beta_{12}}[H_1 + H_2] = \mathbb{E}_{\beta_1}[H_1] + \mathbb{E}_{\beta_2}[H_2]$$

So it makes sense to require that $T \mapsto \beta(T)$ doesn't depend on the system: two systems with the same temperature are in equilibrium with each other.

Ideal gas

Example (Temperature and ideal gas)

We will show that $\mathbb{E}_\beta[H] \sim \beta^{-1}$ in ideal gas. Therefore we set

$$\boxed{\beta = \frac{1}{T}}$$

for all systems.

Ideal gas is N particles of mass m in a box $V = [0,L]^d$, $d = 1,2,3,\dots$ dimension of the space.

State $(\underline{x}, \underline{u}) \in \underbrace{V \times V \times \dots \times V}_{N} \times \underbrace{\mathbb{R}^d \times \mathbb{R}^d \times \dots \times \mathbb{R}^d}_{N}$

$\underline{x}$ positions, $\underline{u}$ momenta.

Hamiltonian

$$H(\underline{x}, \underline{u}) = \sum_{k=1}^{dN} \frac{u_k^2}{2m}$$

Maxwell-Boltzmann distribution

$$\mathbb{P}_\beta[\underline{x} \in A, \underline{u} \in B] = \frac{1}{Z(\beta)} \left(\int_A dx_1 \dots dx_{dN} \right) \left(\int_B \exp(-\beta H(\underline{u}))\, du_1 \dots du_{dN} \right)$$

where the partition function is

$$Z(\beta) = |V|^N \left(\int_{\mathbb{R}^{dN}} \exp(-\beta H(\underline{u}))\, du_1 \dots du_{dN} \right)$$

By making a change of variables $u_k \sqrt{\frac{\beta}{m}} = v_k$ we get

$$Z(\beta) = \left(\frac{\beta}{m} \right)^{-\frac{dN}{2}} I^{dN} |V|^N$$

where $I = \int_{\mathbb{R}} \exp(-\frac{v^2}{2})\, dv = \sqrt{2\pi}$.

Now the internal energy $\mathbb{E}_\beta[H] = -\partial_\beta \log Z(\beta)$

$$\Rightarrow \mathbb{E}_\beta[H] = \frac{d}{2} N \beta^{-1}$$

<u>Example</u> (Ideal gas and pressure)

Let's look at particle 1 and its collitions with walls $x_1 = 0$ and $x_1 = L$.

~~Before~~ ~~Before~~ the particle hits $x_1=0$ its momentum (x_1-component of momentum) is $-|u_1|$ and after $+|u_1|$.

The time it takes the particle to travel from $x_1=0$ to $x_1=L$ and back is $2Lm/|u_1| =: t_0$. The average force that the particle exerts on the wall

$$F_1 = \frac{\int_0^{t_0} F(t)\,dt}{t_0} \overset{\text{Newton's 2nd law}}{=} \frac{\int_0^{t_0} \dot{u}_1(t)\,dt}{t_0}$$

$$= \frac{2|u_1|}{2Lm/|u_1|} = \frac{|u_1|^2}{Lm}$$

Pressure to the wall

$$P = \frac{N\mathbb{E}[F_1]}{\text{Area}} = \frac{N\mathbb{E}[u_1^2]}{m|V|} = \frac{2\mathbb{E}[H]}{d|V|}$$

$$= \frac{N\beta^{-1}}{|V|}$$

Ideal gas state equation $PV = nRT$.