Microcanonical Ensemble

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September 19, 2018

Information and Entropy

- A measure for the lack of information (ignorance): $s_i = -\log P_i = \log \frac{1}{P_i}$.
- An average ignorance: $S = k_B \sum_i P_i s_i = -k_B \sum_i P_i \log P_i = -k_B \langle \log P_i \rangle$.
- We call S as "entropy" (Shannon's Entropy).
- k_B: Boltzmann's constant.

Maximum Entropy

The prior probability distribution maximizes entropy (the average ignorance) while respecting macroscopic constraints. A natural constraint of normalization is $\sum_i P_i = 1$. We have a variational problem

$$\delta \left[S + \lambda (\sum_i P_i - 1) \right] = 0$$

where δ stands for the variation with respect to P. To be specific,

$$\begin{aligned}
\delta \left[S + \lambda (\sum_i P_i - 1) \right] &= \delta \left[-\sum_i P_i \log P_i + \lambda (\sum_i P_i - 1) \right] \\
&= \sum_i \left[-(\delta P_i) \log P_i - P_i (\delta \log P_i) + \lambda (\delta P_i) \right] \\
&= \sum_i \left[-(\delta P_i) \log P_i - P_i \left(\frac{d \log P_i}{d P_i} \delta P_i \right) + \lambda (\delta P_i) \right] \\
&= \sum_i \left[-(\delta P_i) \log P_i - \delta P_i + \lambda (\delta P_i) \right] = 0
\end{aligned}$$

Maximum Entropy

$$\delta\left[S+\lambda(\sum_i P_i-1)\right]=\sum_i\left[-(\delta P_i)\log P_i-\delta P_i+\lambda(\delta P_i)\right]$$
$$=\sum_i\left[(-\log P_i-1+\lambda)\delta P_i\right]=0.$$

It leads

$$-\log P_i-1+\lambda=0.$$

Finally, we get

$$P_i=e^{\lambda-1}=const.\equiv\frac{1}{\Omega}$$

Boltzmann's Entropy

In an equilibrium state, the probability of i state is given by

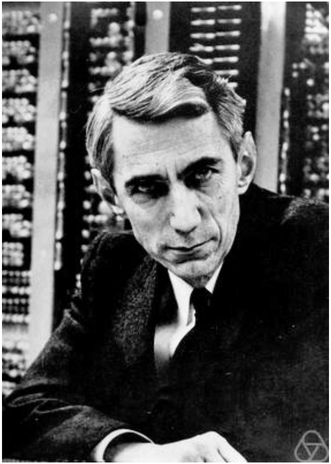
$$p_i = \frac{1}{\Omega}.$$

Then the entropy can be expressed as

$$\begin{aligned} S &= -\langle \log P_i \rangle = -\langle \log \frac{1}{\Omega} \rangle \\ &= \log \Omega. \end{aligned}$$

We will interpret the meaning of entropy later.

Boltzmann and Shannon



Ludwig Boltzmann and Claude Shannon

Microcanonical Ensemble

Fixed energy and the number of particles. We define Ω is the accessible volume in phase space with $E \leq H \leq E + \Delta E$.

$$\Omega = \int_{E \leq H \leq E+\Delta E} dPdQ,$$

where $P = (p_1, p_2, \cdots, p_3N)$ and $Q = (q_1, q_2, \cdots, q_3N)$. The probability and the expectation value is then

$$P = \frac{1}{\Omega},$$
$$\langle O \rangle = \frac{1}{\Omega} \int_{E \leq H \leq E+\Delta E} O(P, Q) dPdQ.$$

Conceptually the microcanonical ensemble approach is extremely simple, in practice it is not so easy.

Ideal Gas in a box

The Hamiltonian of N-ideal gas molecules in a box with volume V:

$$H = \sum_{i}^{3N} \frac{p_i^2}{2m} + V(x_i). \quad (1)$$

where the potential $V(x_i)$ is given by 0 if $x \in V$ and otherwise $V = \infty$. The number (or volume) of states is

$$\begin{aligned} \Omega &= \int_{E \leq H \leq E + \Delta E} dP dQ \\ &= \int dQ \int_{E \leq H \leq E + \Delta E} dP \\ &= \Omega_Q \Omega_P dP \\ &= V^N \Omega(P) \end{aligned}$$

since there is $V = 0$ in a box.

Momentum Space

The constant energy surface is a sphere in $3N$-dimensional space,

$$\sum_{i=1}^{3N} = 2mE = R^2,$$

where radius $R = \sqrt{2mE}$. If we define $\Sigma(E)$ as the volume of region $H \leq E$,

$$\begin{aligned}\Omega_P &= \int_{E \leq H \leq E+\Delta E} dP \\ &= \Sigma(E+\Delta E) - \Sigma(E).\end{aligned}$$

Then, the volume Σ can be computed as

$$\begin{aligned}\Sigma(E) &= \int_{H \leq E} dP \\ &= \int_{\sum_{i=1}^{3N} p_i^2 \leq 2mE} dP\end{aligned}$$

Volume of n-dimensional Sphere

The volume of n-dimensional sphere with radius R is

$$\begin{aligned} V_N(R) &= \int_{\sum_i^N x_i^2 \le R^2} dx_1 dx_2 \cdots dx_N \\ &= R^N \int_{\sum_i^N y_i^2 \le 1} dy_1 dy_2 \cdots dy_N \\ &= R^N C_N, \end{aligned}$$

where $C_N = \int_{\sum_i^N y_i^2 \le 1} dy_1 dy_2 \cdots dy_N$.

$$
\begin{aligned}
I^N = \sqrt{\pi}^N &= \left[\int_{-\infty}^{\infty} e^{-x^2} dx\right]^N \\
&= \int_{-\infty}^{\infty} dx_1 dx_2 \cdots dx_N e^{-(x_1^2+x_2^2+\cdots+x_N^2)} \\
&= \int_{-\infty}^{\infty} dV_N(R) \cdots dx_N e^{-(x_1^2+x_2^2+\cdots+x_N^2)}
\end{aligned}
$$

where $dV_N(R) = dx_1 dx_2 \cdots dx_N = NR^{N-1} C_N dR$. In n-dimensional polar coordinates,

$$
\begin{aligned}
\sqrt{\pi}^N &= \int_0^{\infty} NR^{N-1} C_N e^{-R^2} dR \\
&= C_N \frac{N}{2} \int_0^{\infty} X^{\frac{N}{2}-1} e^{-X} dX = C_N \frac{N}{2} \Gamma\left(\frac{N}{2}\right) \\
&= C_N \Gamma\left(N/2+1\right) = C_N \left(N/2\right)!,
\end{aligned}
$$

where $X = R^2$ and $dX = 2RdR$. Therefore,

$$
C_N = \frac{\pi^{N/2}}{(N/2)!}, \quad V_N(R) = R^N \frac{\pi^{N/2}}{(N/2)!}.
$$

Momentum Space

The volume of region $H \leq E$

$$\begin{aligned}\Omega_P &= \Sigma(E+\Delta E) - \Sigma(E) \\ &= \Delta E \frac{\Sigma(E+\Delta E) - \Sigma(E)}{\Delta E} \\ &\approx \Delta E \frac{d\Sigma(E)}{dE},\end{aligned}$$

where

$$\begin{aligned}\frac{d\Sigma(E)}{dE} &= \frac{d}{dE}\frac{\pi^{3N/2}(2mE)^{3N/2}}{(3N/2)!} \\ &= \frac{3N}{2}\frac{\pi^{3N/2}(2mE)^{3N/2-1}}{(3N/2)!} \\ &= \frac{(2\pi m)^{3N/2}E^{3N/2-1}}{(3N/2-1)!}\end{aligned} \tag{2}$$

Number of States & Entropy

The total number (volume) of states is

$$\Omega = V^N \Delta E \frac{(2\pi m)^{3N/2} E^{3N/2-1}}{(3N/2-1)!} \tag{3}$$

The entropy is then $k_B \log \Omega$, and

$$\begin{aligned}\log \Omega &= \log V^N + \log \Delta E + \frac{3N}{2} \log(2\pi m) \\ &+ \left(\frac{3N}{2} - 1\right) \log E - \log(3N/2-1)! \\ &\approx N \log V + \frac{3N}{2} \log(2\pi m E) - (3N/2)\log(3N/2) + (3N/2)\end{aligned}$$

Entropy for Ideal Gas

The entropy is

$$S \approx Nk_B \log V + \frac{3Nk_B}{2} \log(2\pi m E) - (3Nk_B/2)\log(3N/2) + (3Nk_B/2).$$

$$\begin{aligned}\frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk_B}{2E}, \\ \frac{P}{T} &= \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk_B}{V}.\end{aligned}$$

Therefore, we can derive equipartition theorem and the equation of state for the ideal gas,

$$E = \frac{3}{2}Nk_BT, \quad PV = Nk_BT.$$