

Microcanonical Ensemble

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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 $\sum_i P_i = 1$. Applying the Lagrange multiplier method,

$$\nabla[S + \lambda(\sum_i P_i - 1)] = 0,$$

where ∇ stands for the derivative with respect to P . To be specific,

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

Maximum Entropy

It leads

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

Finally, we get

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

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 see 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 $E \leq H \leq E + \Delta E$.

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

where $P = (p_1, p_2, \dots, p_{3N})$ and $Q = (q_1, q_2, \dots, q_{3N})$. The probability and the expectation value is then

$$P = \frac{1}{\Omega},$$

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

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 (i.e, helium atoms at high temperatures and low densities):

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

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

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

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

Momentum Space

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

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

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

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

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

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

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

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

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

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

(2)

Number of States & Entropy

The total number (volume) of states is

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

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

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

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{3Nk_B}{2E},$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{Nk_B}{V}.$$

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

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

Gibbs Paradox

Compare $2N$ particles in two boxes with volume V and $2N$ particles in a box with volume $2V$:

$$S_1 = 2k_B \log V^N,$$

$$S_2 = k_B \log(2V)^{2N}.$$

Gibbs Paradox & Gibbs factor

All particles are perfectly identical or indistinguishable:

$$S_1 = 2k_B \log V^N / N!,$$

$$S_2 = k_B \log (2V)^{2N} / (2N)!.$$

Planck Constant

- h has the unit of momentum \times distance.
- The uncertainty principle: $\delta x \delta p \geq h$.

Applying two factors, we find the Sackur-Tetrode formula:

$$\Omega = \Omega_{crude} / (N! h^{3n}).$$

$$S(N, V, E) = Nk_B \log \left[\frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} \right] + Nk_B \frac{5}{2}. \quad (4)$$