

Canonical Ensemble

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Boltzmann's Distribution

Canonical Ensemble describes an equilibrium system which can exchange energy with a heat bath at a known temperature T . Hence, its energy E_s is not confined and conserved. And, any energy is allowed. But, the probability distribution $P(E_s)$ depending on its energy E is no longer uniform but is $P(E_s) \sim e^{-\beta E_s}$.

Maximum Entropy

The prior probability distribution maximizes entropy while respecting macroscopic constraints. Now, we have two constraints: normalization $\sum_i P_i = 1$ and average energy $\sum_i P_i E_i = \langle E \rangle$. Applying the Lagrange multiplier method,

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

Maximum Entropy

It leads

$$-\log P_i - 1 - \lambda - \beta E_i = 0.$$

Thus,

$$P_i \sim e^{-\beta E_i},$$

and finally we obtain

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{1}{Z} e^{-\beta E_i},$$

where the normalization factor Z is called as “partition function”,

$$Z = \sum_i e^{-\beta E_i}. \quad (1)$$

Contact to Heat Bath

Assuming that the composite system of heat bath and the system of interest is isolated, the distribution for the energy in the system is

$$P(E) = \frac{\Omega(E)\Omega_B(E_B)}{\Omega_T(E + E_B)},$$

where Ω_B is the number of state for the energy in the heat bath and Ω_T is the number of state for the energy in the total system. Taking the logarithm,

$$\log P(E) = \log \Omega(E) + \log \Omega_B(E_T - E) - \log \Omega_T(E_T),$$

where $E_T = E + E_B$. Expand $\log \Omega_B$ in powers of E ,

$$\log P(E) \approx \log \Omega(E) + \log \Omega_B(E_T) - \left(\frac{\partial \log \Omega_B(E_T)}{\partial E_T} \right) E - \log \Omega_T(E_T).$$

Contact to Heat Bath

$$\begin{aligned}\log P(E) &\approx \log \Omega(E) + \log \Omega_B(E_T) - \left(\frac{\partial \log \Omega_B(E_T)}{\partial E_T} \right) E - \log \Omega_T(E_T) \\ &= \log \Omega(E) - E \left(\frac{1}{k_B} \frac{\partial S_B(E_T)}{\partial E_T} \right) + \log \Omega_B(E_T) - \log \Omega_T(E_T) \\ &= \log \Omega(E) - \beta E - \log Z,\end{aligned}$$

where $\beta = \frac{1}{k_B} \frac{\partial S_B(E)}{\partial E}$. Finally we obtain canonical distribution again,

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{1}{Z} e^{-\beta E_i}.$$

Temperature

What is β in the previous calculation? Consider two energetically connected systems. Note that

$$P_1(E_1) = \frac{\Omega_1(E_1)\Omega_2(E - E_1)}{\Omega_T(E)},$$
$$P_2(E_2) = \frac{\Omega_2(E_2)\Omega_1(E - E_2)}{\Omega_T(E)}.$$

At the equilibrium, P_1 (P_2) is a very sharply peaked function near its maximum at E_1^* (E_2^*). Thus, we have

$$\frac{d\Omega_1(E_1)\Omega_2(E - E_1)}{dE_1} = 0.$$

Temperature

$$\begin{aligned}\frac{d\Omega_1(E_1)\Omega_2(E - E_1)}{dE_1} &= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E - E_1) + \Omega_1(E_1)\frac{d\Omega_2(E - E_1)}{dE_1} \\ &= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E - E_1) + \Omega_1(E_1)\frac{d\Omega_2(E - E_1)}{dE_1} \\ &= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2} = 0.\end{aligned}$$

Therefore, we find that

$$\begin{aligned}\frac{1}{\Omega_1} \frac{d\Omega_1(E_1)}{dE_1} &= \frac{1}{\Omega_2} \frac{d\Omega_2(E_2)}{dE_2} \\ \frac{dS_1}{dE} &= \frac{dS_2}{dE}.\end{aligned}$$

At equilibrium, $\frac{dS_1}{dE}$ is constant and we define it as

$$\frac{1}{T} = \frac{\partial S}{\partial E}. \quad (2)$$

Short Summary of Canonical Ensemble

$$P_i = \frac{1}{Z} e^{-\beta E_i},$$
$$Z = \sum_i e^{-\beta E_i},$$
$$\beta = \frac{1}{k_B} \frac{\partial S}{\partial E} = \frac{1}{k_B T}.$$

Partition function

The partition function is

$$Z = \sum_i e^{-\beta E_i}.$$

- The partition function Z is just the normalization factor.
- At the same time, the partition function Z is **not** just the normalization factor.

Let us see how to calculate the average energy, the specific heat and the entropy by using Z .

Average Energy & Specific Heat

The average energy $\langle E \rangle$ is given by

$$\begin{aligned}\langle E \rangle &= \sum_i P_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = -\frac{1}{Z} \frac{\partial \sum_i e^{-\beta E_i}}{\partial \beta} \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta}.\end{aligned}$$

The specific heat c_v at constant volume is

$$\begin{aligned}Nc_v &= \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T} \\ &= -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta} = \frac{1}{k_B T^2} \frac{\partial^2 \log Z}{\partial \beta^2}.\end{aligned}$$

Entropy

The entropy is $S = -k_B \sum_i P_i \log P_i$. Thus,

$$\begin{aligned} S &= -k_B \sum_i P_i \log P_i \\ &= -k_B \sum_i \frac{e^{-\beta E_i}}{Z} \log \left[\frac{e^{-\beta E_i}}{Z} \right] \\ &= -\frac{k_B}{Z} \sum_i e^{\beta E_i} [-\beta E_i - \log Z] \\ &= k_B \beta \langle E \rangle + k_B \log Z \\ &= \frac{\langle E \rangle}{T} + k_B \log Z. \end{aligned}$$

Free Energy

The Helmholtz free energy can be defined by using Z :

$$S = \frac{\langle E \rangle}{T} + k_B \log Z,$$
$$A = -k_B T \log Z = \langle E \rangle - TS.$$

The free energy is the energy available to do work. In addition, the entropy is minus the derivative of A with respect to T ,

$$\begin{aligned} \frac{\partial A}{\partial T} &= \frac{\partial -k_B T \log Z}{\partial T} \\ &= -k_B \log Z - k_B T \frac{\partial \log Z}{\partial \beta} \frac{\partial \beta}{\partial T} \\ &= -k_B \log Z - k_B T \langle E \rangle \frac{1}{k_B T^2} \\ &= -k_B \log Z - \frac{\langle E \rangle}{T} = -S. \end{aligned}$$

Fluctuation of Energy and Susceptibility

Consider again the specific heat c_v at constant volume.

$$\begin{aligned} Nc_v &= \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T} \\ &= -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta} \\ &= -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \\ &= -\frac{1}{k_B T^2} \left[\frac{\sum_i -E_i^2 e^{\beta E_i}}{Z} + \frac{(\sum_i E_i e^{-\beta E_i})^2}{Z^2} \right] \\ &= \frac{1}{k_B T^2} [\langle E^2 \rangle - \langle E \rangle^2] \end{aligned}$$

Microcanonical Ensemble and Canonical Ensemble

Defining energy fluctuation $\sigma_E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$ per particle, since $Nc_v = \frac{\sigma_E^2}{k_B T^2}$ the energy fluctuation is given as

$$\begin{aligned}\sigma_E/N &= \sqrt{\langle E^2 \rangle - \langle E \rangle^2}/N \\ &= \sqrt{(k_B T)(c_v T)}/\sqrt{N}.\end{aligned}$$

The fluctuation will not change the macroscopic properties at the thermodynamics limit $N \rightarrow \infty$ because

$$\sigma_E/N \sim \frac{1}{\sqrt{N}}.$$

Therefore, the constant energy (microcanonical ensemble) and constant temperature (canonical ensemble) predict the same macroscopic behavior.