# Canonical Ensemble

Byungjoon Min

Department of Physics, Chungbuk National University

October 29, 2018

# 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,

$$\frac{\partial}{\partial P} \left[ S - \lambda(\sum_i P_i - 1) - \beta(\sum_i P_i E_i - \langle E \rangle) \right]$$

$$= \frac{\partial}{\partial P} \left[ -\sum_i P_i \log P_i - \lambda(\sum_i P_i - 1) - \beta(\sum_i P_i E_i - \langle E \rangle) \right]$$

$$= \sum_i \left[ -\log P_i - P_i \frac{d \log P_i}{dP_i} - \lambda - \beta \sum_i E_i \right]$$

$$= \sum_i \left[ -\log P_i - 1 - \lambda - \beta E_i \right] = 0.$$

# 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",

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

# 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 $\Omega_B$ is the number of state for the energy in the heat bath and $\Omega_T$ 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

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

$$= \log \Omega(E) - E\left(\frac{1}{k_B}\frac{\partial S_B(E_T)}{\partial E_T}\right) + \log \Omega_B(E_T) - \log \Omega_T(E_T)$$

$$= \log \Omega(E) - \beta E - \log Z,$$

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 $\beta$ 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

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

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

$$= \frac{d\Omega_1(E_1)}{dE_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{d\Omega_2(E_2)}{dE_2} = 0.$$

Therefore, we find that

$$\frac{1}{\Omega_1}\frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2}\frac{d\Omega_2(E_2)}{dE_2}$$

$$\frac{dS_1}{dE} = \frac{dS_2}{dE}.$$

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

$$\frac{1}{T} = \frac{\partial S}{\partial E}. \tag{2}$$

# 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

$$\langle E \rangle = \sum_i P_i E_i = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = -\frac{1}{Z} \frac{\partial \sum_i e^{-\beta E_i}}{\partial \beta}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta}.$$

The specific heat $c_v$ at constant volume is

$$Nc_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T}$$

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

# Entropy

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

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

# 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.

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

# Microcanonical Ensemble and Canonical Ensemble

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

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

The fluctuation will not change the macroscopic properties at the thermodynamics limit $N \to \infty$ 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.

# Summary of Canonical Ensemble

- Write down the partition function, $Z = \sum_i e^{-\beta E_i}$.
- Evaluate thermodynamic quantities.
- The free energy $A = -k_B T \log Z = \langle E \rangle - TS$.

Also note that the partition function can be expressed in different forms:

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

$$Z = \frac{1}{h^{3N}} \int e^{-\beta E(q,p)} dq dp,$$

$$Z = \int g(E) e^{-\beta E} dE.$$

# Classical Gas

The Hamiltonian is given by $H = \frac{p^2}{2m} + V(r)$.

$$
\begin{aligned}
Z &= \frac{1}{h^{3N} N!} \int e^{-\beta E(q,p)} dq dp \\
&= \frac{1}{h^{3N} N!} \int dq dp \, e^{-\beta \left[ \sum_i^N \frac{p^2}{2m} + \sum_i^N \sum_{i>j}^N V(r_i, r_j) \right]} \\
&= \frac{1}{h^{3N} N!} \int dp \, e^{-\beta \left[ \sum_i^N \frac{p^2}{2m} \right]} \int dq \, e^{\left[ -\beta \sum_i^N \sum_{i>j}^N V(r_i, r_j) \right]} \\
&= \frac{1}{h^{3N} N!} \left( \frac{2\pi m}{\beta} \right)^{3N/2} \int dq \, e^{\left[ -\beta \sum_i^N \sum_{i>j}^N V(r_i, r_j) \right]}.
\end{aligned}
$$

# Classical Ideal Gas

The Hamiltonian is given by $H = \frac{p^2}{2m}$.

$$Z = \frac{1}{h^{3N}N!} \int dq\,dp\ e^{-\beta\left[\sum_i^N \frac{p^2}{2m}\right]}$$

$$= \frac{1}{h^{3N}N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \int dq$$

$$= \frac{1}{h^{3N}N!} \left(\frac{2\pi m}{\beta}\right)^{3N/2} V^N.$$

Note that $Z = (Z_1)^N$ since there are no interactions. Then, all thermodynamic quantities can be derived from $Z$, such as

$$A = -k_B T \log Z, \ \langle E \rangle = -\frac{\partial \log Z}{\partial \beta}, \ Nc_v = \frac{\partial \langle E \rangle}{\partial T}.$$

# Harmonic Oscillator

The Hamiltonian is given by $H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2$.

$$Z_1 = \frac{1}{h} \int dq dp \ e^{-\beta\left[\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\right]}$$

$$= \frac{1}{h}\sqrt{\frac{2\pi m}{\beta}}\sqrt{2\pi}\beta m\omega^2$$

$$= \frac{2\pi}{h\beta\omega} = \frac{1}{\beta\hbar\omega}.$$

Then, all thermodynamic quantities can be derived from $Z$, such as

$$A = -k_B T \log Z, \ \langle E \rangle = -\frac{\partial \log Z}{\partial \beta}, \ N c_v = \frac{\partial \langle E \rangle}{\partial T} = Nk.$$

# (Quantum) Harmonic Oscillator

Energy is $\hbar\omega\left(n + \frac{1}{2}\right)$. Thus,

$$Z_1 = \sum_n e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)}$$

$$= e^{-\beta\hbar\omega/2} \sum_n^\infty \left(e^{-\beta\hbar\omega}\right)^n$$

$$= e^{-\beta\hbar\omega/2} \frac{1}{1 - e^{-\beta\hbar\omega}}$$

$$= \frac{1}{2\sinh(\beta\hbar\omega/2)}.$$

Then, all thermodynamic quantities can be derived from $Z$, such as

$$A = -k_B T \log Z, \ \langle E \rangle = -\frac{\partial \log Z}{\partial \beta}, \ N c_v = \frac{\partial \langle E \rangle}{\partial T}.$$

# Two Level System

Energy spectrum of a two level system is given by $E_0 = -\epsilon$ and $E_1 = +\epsilon$.

$$Z_1 = \sum_n e^{-\beta E_n}$$
$$= e^{-\beta(-\epsilon)} + e^{-\beta\epsilon}$$
$$= 2\cosh(\beta\epsilon)$$

Then, all thermodynamic quantities can be derived from $Z$, such as

$$A = -k_B T \log Z, \ \langle E \rangle = -\frac{\partial \log Z}{\partial \beta}, \ Nc_v = \frac{\partial \langle E \rangle}{\partial T}.$$