Comparison between micro-canonical and canonical ensembles and basic formulas for statistical mechanics

	Micro-canonical Ensemble	Canonical Ensemble
Macroscopic Independent Variables	N, E, V	N, T, V
Partition Functions	$W(N, E, V, \delta E) = \Omega(N, E, V)\delta E$	$Z_C = \sum_{l_N} e^{-\beta E_{l_N}}$
Probability Distribution Functions	$f = \frac{\delta(E - E_l)\delta E}{W}$	$f = \frac{1}{Z} e^{-\beta E_{l_N}}$
Entropy	$S = k_B \log W$	$S = k_B(1 + T\frac{\partial}{\partial V})\log Z$
Helmholtz Free Energy	$F = E - k_B T \log W$	$F = -k_B T \log Z$
Gibbs Free Energy	$G = E - k_B(1 - V\frac{\partial}{\partial V})\log W$	$G = -k_B(1 - V\frac{\partial}{\partial V})\log Z$
Internal Energy	E(given)	$E = -\frac{\partial}{\partial \beta}\log Z$
Temperature	$T = [k_B \frac{\partial}{\partial E}\log W]^{-1}$	T(given)
Pressure	$P = k_B T \frac{\partial}{\partial V}\log W$	$P = k_B T \frac{\partial}{\partial V}\log Z$
Chemical Potential	$\mu = -k_B T \frac{\partial}{\partial N}\log W$	$\mu = -k_B T \frac{\partial}{\partial N}\log Z$
Energy Fluctuation	$\Delta E = 0$	$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2}\log Z$

Micro-canonical Ensemble

The number of possibility: (Bosons)

$M \longrightarrow$ total quantum number for each system, and

$N \longrightarrow$ the total number of the independent systems:

$$W_M = \frac{(M + N - 1)!}{M!(N - 1)!}$$

The number of possibility: (Fermions)

$M \longrightarrow$ total quantum number for each system, and

$N \longrightarrow$ the total number of the independent systems:

$$W_M = \frac{N!}{M!(N - M)!}$$

The number of possibility: (Maxwell-Boltzmann)

$M \longrightarrow$ total quantum number for each system, and

$N \longrightarrow$ the total number of the independent systems:

$$W_M = N^M$$

Basic Relationships

Entropy:

$$S = k \log W_M$$

Temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S}{\partial M} \frac{\partial M}{\partial E}$$

Heat Capacity:

$$C = \frac{\partial E}{\partial T}$$

Partition Function for Canonical Ensemble:

$$\text{Classical} \quad Z \; = \; \frac{1}{\prod N! h^{dN}} \iint \exp(-\beta E) \, dq \, dp$$

$$\text{Quantum} \quad Z \; = \; \sum_l \exp(-\beta E_{N,l})$$

where d is the spatial dimension of the system and $\beta = (kT)^{-1}$.

Helmholtz Free Energy and the related relationships:

$$
\begin{aligned}
\text{The Free Energy} \quad & F \; = \; -kT \log Z \\
\text{The Entropy} \quad & S \; = \; -\frac{\partial F}{\partial T} \\
\text{The Pressure} \quad & P \; = \; -\frac{\partial F}{\partial V} \\
\text{The Internal Energy} \quad & U \; = \; -T^2 \frac{\partial \left(\frac{F}{T}\right)}{\partial T}
\end{aligned}
$$

An Example for Obtaining a Partition Function

Consider the one-dimensional classical and quantum harmonic oscillator. The Hamiltonian is:

$$H = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}$$

Using gaussian integral, $\int_{-\infty}^{\infty} \exp(-\alpha x^2)dx = \sqrt{\frac{\pi}{\alpha}}$, we obtain the classical partition function:

$$Z = \frac{1}{h} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp(-\beta H)dqdp = \frac{2\pi}{\beta h \omega} = \frac{2\pi kT}{h\omega}$$

Note that $N = 1$ and $d = 1$.

For the quantum partition function, the energy eigenvalues are expressed as

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu$$

Thus, we can calculate it as follows:

$$
\begin{aligned}
Z &= \sum_n \exp\left[\beta\left(n + \frac{1}{2}\right)h\nu\right] \\
&= \exp\left[\frac{-\beta h\nu}{2}\right] \sum_n \left\{\exp\left[-\beta h\nu\right]\right\}^n
\end{aligned}
$$

Use

$$\sum_n = \left\{\exp\left[-x\right]\right\}^n = \frac{1}{1 - \exp[-x]}$$

Then,

$$
\begin{aligned}
Z &= \frac{\exp[\frac{-\beta h\nu}{2}]}{1 - \exp[\frac{-\beta h\nu}{2}]} \\
&= \frac{1}{\exp[\frac{\beta h\nu}{2}] - \exp[\frac{-\beta h\nu}{2}]} \\
&= \frac{1}{2\sinh\left(\frac{\beta h\nu}{2}\right)}
\end{aligned}
$$