Formula of Canonical ensemble

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Here we present the formula for the canonical ensemble for the convenience.

The internal energy U:

$$U = -\frac{\partial \ln Z_C}{\partial \beta} = -\frac{1}{\frac{\partial \beta}{\partial T}}\frac{\partial \ln Z_C}{\partial T} = k_B T^2 \frac{\partial \ln Z_C}{\partial T}.$$

since

$$\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = \frac{1}{\frac{\partial \beta}{\partial T}}\frac{\partial}{\partial T} = -k_B T^2$$

The pressure P:

$$P = \sum_i P_i \frac{1}{Z_C} e^{-\beta E_i} = \frac{1}{Z_C}\sum_i \left(-\frac{\partial E_i}{\partial V}\right) e^{-\beta E_i} = \frac{1}{Z_C}\frac{1}{\beta}\frac{\partial Z_C}{\partial V} = \frac{1}{\beta}\frac{\partial \ln Z_C}{\partial V}$$

The Helmholtz free energy F as

$$F = E - ST.$$

$$\begin{aligned} dF &= dE - SdT - TdS \\ &= TdS - PdV - SdT - TdS \\ &= -PdV - SdT \end{aligned}$$

F is a function of T and V; $F = F(T, V)$. From the equation of dF, we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

Helmholtz free energy F:

$$F = -k_B T \ln Z_C$$

$$\frac{\partial}{\partial T}(\frac{F}{T}) = \frac{T\frac{\partial F}{\partial T} - F}{T^2} = \frac{-ST - F}{T^2} = -\frac{U}{T^2} = -k_B \frac{\partial}{\partial T}\ln Z_C ,$$

which leads to

$$F = -k_B T \ln Z_C$$

The entropy S in a canonical ensemble

$$S = \frac{U - F}{T}$$

where U is the average energy of the system,

$$U = -\frac{\partial \ln Z_C}{\partial \beta}$$

Then entropy S is written as

$$S = -k_B \beta \frac{\partial \ln Z_C}{\partial \beta} + k_B \ln Z_C$$

or

$$\begin{aligned}
S &= -\frac{1}{T}\frac{\partial \ln Z_C}{\partial \beta} + k_B \ln Z_C \\
&= \frac{1}{T}\frac{1}{Z_C}\sum_i E_i e^{-\beta E_i} + k_B \ln Z_C \\
&= k_B \beta \sum_i E_i \frac{e^{-\beta E_i}}{Z_C} + k_B \ln Z_C \\
&= k_B \sum_i \beta E_i p_i + k_B \ln Z_C \\
&= k_B \sum_i (-\ln p_i - \ln Z_C) p_i + k_B \ln Z_C \\
&= -k_B \sum_i p_i \ln p_i
\end{aligned}$$

or

$$S = -k_B \sum_i p_i \ln p_i ,$$

where p_i is that the probability of the $\left|i\right\rangle$ state and is given by

$$p_i = \frac{1}{Z_C} e^{-\beta E_i}$$

The logarithm of p_i is described by

$$\ln p_i = -\beta E_i - \ln Z_C$$

Here we have

$$\begin{aligned} S &= -k_B \sum_i p_1 \ln p_i = -k_B \sum_i p_1 (-\beta E_i - \ln Z_C) \\ &= -k_B (-\beta U - \ln Z_C) \\ &= \frac{U}{T} + k_B \ln Z_C \end{aligned}$$

or

$$TS = U + k_B T \ln Z_C$$

or

$$F = U - ST = -k_B T \ln Z_C$$

We start with the expression (Fermi)

$$dU = TdS - PdV = d(TS) - SdT - PdV$$

or

$$d(U - TS) = dF = -SdT - PdV$$

with

$$F = U - ST \qquad \text{or} \qquad S = \frac{U}{T} - \frac{F}{T}$$

Note that

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

At constant V, we get

$$dS = \frac{1}{T}dU = k_B\beta dU = k_B[d(\beta U) - Ud\beta]$$

Using the relation

$$U = -\frac{\partial}{\partial\beta}\ln Z$$

we have

$$\begin{aligned}S &= \int \frac{1}{T}dU \\ &= \int k_B\beta dU \\ &= \int k_B[d(\beta U) - Ud\beta]\end{aligned}$$

or

$$\begin{aligned}S &= k_B\beta U + k_B\int \frac{\partial}{\partial\beta}(\ln Z)d\beta \\ &= k_B\beta U + k_B\ln Z \\ &= \frac{U}{T} + k_B\ln Z\end{aligned}$$

or

$$\frac{F}{T} = \frac{U}{T} - S = -k_B\ln Z$$

The Helmholtz free energy is

$$F = -k_BT\ln Z = -\frac{1}{\beta}\ln Z$$

The entropy S is

$$S = k_B[\ln Z - \beta\frac{\partial}{\partial\beta}\ln Z] = -k_B\beta^2\frac{\partial}{\partial\beta}(\frac{1}{\beta}\ln Z)$$

This expression of S can be also derived as

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_V \\ &= -\frac{\partial \beta}{\partial T}\left(\frac{\partial F}{\partial \beta}\right)_V \\ &= k_B \beta^2 \left(\frac{\partial F}{\partial \beta}\right)_V \\ &= -k_B \beta^2 \frac{\partial}{\partial \beta}\left(\frac{1}{\beta}\ln Z\right) \end{aligned}$$

or

$PV = \frac{2}{3}U$ for ideal gas

$PV = \frac{1}{3}U$ for ideal photon gas

Energy fluctuation:

$$Z_C = \sum_i e^{-\beta E_i}$$

$$\frac{\partial Z_C}{\partial \beta} = -\sum_i E_i e^{-\beta E_i}, \qquad \frac{\partial^2 Z_C}{\partial \beta^2} = \sum_i (-E_i)^2 e^{-\beta E_i} = \sum_i E_i^{\,2} e^{-\beta E_i}$$

$$\langle E \rangle = U = \frac{1}{Z_C}\sum_i E_i e^{-\beta E_i} = -\frac{1}{Z_C}\frac{\partial Z_C}{\partial \beta} = -\frac{\partial \ln Z_C}{\partial \beta},$$

$$\langle E^2 \rangle = \frac{1}{Z_C}\sum_i E_i^{\,2} e^{-\beta E_i} = \frac{1}{Z_C}\frac{\partial^2 Z_C}{\partial \beta^2}$$

$$
\begin{aligned}
(\Delta E)^2 &= \langle (E - \langle E \rangle)^2 \rangle \\
&= \langle E^2 \rangle - \langle E \rangle^2 \\
&= \frac{1}{Z}\frac{\partial^2 Z_C}{\partial \beta^2} - \frac{1}{Z_C{}^2}\left(\frac{\partial Z_C}{\partial \beta}\right)^2 \\
&= \frac{\partial^2 \ln Z_C}{\partial \beta^2}
\end{aligned}
$$

or

$$(\Delta E)^2 = -\frac{\partial}{\partial \beta}U = k_B T^2 \frac{\partial}{\partial T}U = k_B T^2 C$$

where C is the heat capacity.

Similarly we have

$$(\Delta E)^n = (-1)^n \frac{\partial^n \ln Z_C}{\partial \beta^n}$$

Since $(\Delta E)^2$ can never be negative, it follows that $\frac{\partial}{\partial \beta}\langle E \rangle \leq 0$ (or equivalently, that $\frac{\partial}{\partial T}\langle E \rangle \geq 0$).

$$(\Delta E)^2 = k_B T^2 C \propto N, \qquad \langle E \rangle \propto N$$

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

In the limit of $N \to \infty$ (thermodynamic limit), the energy fluctuation becomes zero.