Formula for the canonical and grand canonical ensembles

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(a) The canonical ensemble

$$Z_C = \sum_i \exp(-\beta E_i)$$

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

$$U = -T^2 \frac{\partial}{\partial T}(\frac{F}{T})|_V$$

The Helmholtz free energy

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

$$dF = dU - d(ST) = TdS - PdV - SdT - TdS = -PdV - SdT$$

The pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T\left(\frac{\partial \ln Z_C}{\partial V}\right)_T$$

The entropy:

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

The fluctuation:

$$
(\Delta E)^2 = \frac{1}{Z_C} \frac{\partial^2 Z_C}{\partial \beta^2}
$$

(b) Grand canonical ensemble

$$
\begin{aligned}
Z_G &= \sum_{N=0}^{\infty} \sum_{i[N]} \exp[\beta(\mu N - E_i(N)] \\
&= \sum_{N=0}^{\infty} \sum_{i[N]} z^N \exp(-\beta E_i(N)] \\
&= \sum_{N=0}^{\infty} z^N \sum_{i[N]} \exp(-\beta E_i(N)] \\
&= \sum_{N=0}^{\infty} z^N Z_{CN}
\end{aligned}
$$

with

$$
Z_G = \sum_N z^N Z_{CN}
$$

where

$$
Z_{CN} = \sum_{i[N]} \exp(-\beta E_i(N)]
$$

$$\langle N \rangle = k_B T \frac{\partial}{\partial \mu} \ln Z_G$$

Grand potential

$$\Phi_G = -k_B T \ln Z_G , \qquad PV = k_B T \ln Z_G$$

$$\Phi_G = -PV = F - \mu N = U - ST - \mu N$$

The pressure

$$P = k_B T \frac{\partial}{\partial V} \ln Z_G$$

$$U - \mu N = -T^2 \frac{\partial}{\partial T} \left(\frac{\Phi_G}{T} \right)_{V,\mu}$$

$$\begin{aligned} d\Phi_G &= dU - d(ST) - d(\mu N) \\ &= TdS - PdV + \mu dN - SdT - TdS - \mu dN - Nd\mu \\ &= -PdV - SdT - Nd\mu \end{aligned}$$

$$S = -\left(\frac{\partial \Phi_G}{\partial T} \right)_{V,\mu} , \qquad P = -\left(\frac{\partial \Phi_G}{\partial V} \right)_{T,\mu} , \qquad N = -\left(\frac{\partial \Phi_G}{\partial \mu} \right)_{T,V}$$

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{\langle N \rangle k_B T}{\rho} \left(\frac{\partial \rho}{\partial \mu} \right)_T$$

$$(\Delta N)^2 = (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial^2 \mu}$$

((**Note**))

We use Φ_G as grand potential, instead of *J*.

Gibbs free energy:

$$G = F + PV = \Phi_G + \mu N + PV = \mu N$$

Helmholtz free energy:

$$F = \Phi_G + \mu N$$

$$dF = -SdT - PdV + \mu dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

Magnetization and susceptibility

$$Z = Tr[e^{-\beta\hat{H}}]$$

$$\frac{\partial Z}{\partial B} = Tr[-\beta\frac{\partial \hat{H}}{\partial B}e^{-\beta\hat{H}}]$$
$$= \beta Tr[\hat{M}e^{-\beta\hat{H}}]$$

where

$$\hat{H} = -\hat{M}\cdot B$$

The average magnetization:

$$\langle M \rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial B} = \frac{1}{\beta}\frac{Z'}{Z}$$

$$\frac{\partial^2 Z}{\partial B^2} = \beta^2 Tr[\hat{M}^2 e^{-\beta \hat{H}}] = \beta^2 Z \langle \hat{M}^2 \rangle$$

or

$$\langle \hat{M}^2 \rangle = \frac{1}{\beta^2}\frac{Z''}{Z}$$

The fluctuation of magnetization:

$$\begin{aligned}(\Delta M)^2 &= \langle \hat{M}^2 \rangle - \langle \hat{M} \rangle^2 \\ &= \frac{1}{\beta^2}\left(\frac{Z''Z - Z'^2}{Z^2}\right) \\ &= \frac{1}{\beta^2}\frac{d}{dB}\frac{Z'}{Z} \\ &= \frac{1}{\beta^2}\frac{d^2}{dB^2}\ln Z\end{aligned}$$

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water

$L_f = 334$ kJ/kg (Latent heat for fusion)

$L_f = 2260$ kJ/kg (Latent heat for vaporization)

cal= 4.1855 J

$$PV = \frac{2}{3}U$$ (non-relativistic case)

$$PV = \frac{1}{3}U$$ (ultra-relativistic case)

(Bellac)