Grand canonical ensemble; Formula

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date: November 27, 2018)

Gibbs factor:

$$P = \frac{1}{Z_G} \exp[\beta(\mu N - E)]$$

where μ is the chemical potential and $\beta = \frac{1}{k_B T}$.

The partition function Z_G:

$$Z_G = \exp(-\beta \Phi_G)$$

$$Z_G = \sum_{N=0} \sum_{i(N)} z^N e^{-\beta E_i(N)} = \sum_{N=0} z^N \sum_{i(N)} e^{-\beta E_i(N)} = \sum_{N=0} z^N Z_{CN}$$

with

$$Z_{CN} = \sum_{i(N)} e^{-\beta E_i(N)}$$

The grand potential:

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

The fugacity (or the absolute activity):

$$z = e^{\beta\mu}$$

The internal energy:

$$U = \mu \langle N \rangle_G - \frac{\partial}{\partial \beta} \ln Z_G = \frac{1}{\beta} \mu \frac{\partial \ln Z_G}{\partial \mu} - \frac{\partial}{\partial \beta} \ln Z_G$$

$$\frac{\partial}{\partial \mu} \ln Z_G = \beta \langle N \rangle_G$$

$$\langle N \rangle_G = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln Z_G = z\frac{\partial}{\partial z}\ln Z_G$$

The entropy:

$$S = k_B(\ln Z_G - \beta\frac{\partial}{\partial \beta}\ln Z_G)$$

$$S = \frac{\partial}{\partial T}\left(\frac{1}{\beta}\ln Z_G\right) = -k_B\beta^2\frac{\partial}{\partial \beta}\left(\frac{1}{\beta}\ln Z_G\right).$$

The pressure:

$$p = \frac{\partial}{\partial V}\left(\frac{1}{\beta}\ln Z_G\right)$$

The average number:

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

The Helmholtz free energy:

$$F = \mu\langle N \rangle_G - k_B T\ln Z_G$$

or

$$F = -k_B T(\ln Z_G - \frac{\partial \ln Z_G}{\partial \ln \mu})$$

When we use $\bar{N} = \langle N \rangle_G$ for simplicity, we have

$$\Phi_G = F - \mu\bar{N}$$

The Gibbs free energy:

$$G = \mu \langle N \rangle_G$$

or

$$G = G(T, P, N) = \mu \langle N \rangle_G = \mu z \frac{\partial}{\partial z} \ln Z_G$$

$$\Phi_G = F - \mu \langle N \rangle_G = -k_B T \ln Z_G = -PV$$

Note

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

We also note that

$$d(\frac{\Phi_G}{T}) = -\frac{(U - \mu \langle N \rangle_G)}{T^2} dT - \frac{P}{T} dV - \frac{\langle N \rangle_G}{T} d\mu$$

which leads to the relation

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

and

$$U = \mu \langle N \rangle_G - \frac{\partial}{\partial \beta} \ln Z_G$$

with

$$\Phi_G = -k_B T \ln Z_G$$

Average number:

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

or

$$\langle N \rangle_G = \frac{z}{Z_G}\frac{\partial Z_G}{\partial z} = z\frac{\partial \ln Z_G}{\partial z}$$

Variance in the number

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

$$\begin{aligned}(\Delta N)^2 &= \langle N^2 \rangle_G - \langle N \rangle_G{}^2 \\ &= (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2}\end{aligned}$$

$$(\Delta N)^2 = k_B T \left(\frac{\partial \langle N \rangle_G}{\partial \mu}\right)_{T,V} = z\frac{\partial}{\partial z}\langle N \rangle_G$$

Part II Approximation from GCE to Canonical ensemble

We assume that

$$Z_G \approx (z)^{\bar{N}} Z_{C\bar{N}}$$

$$\begin{aligned}\langle N \rangle_G &= z\frac{\partial}{\partial z}\ln Z_G \\ &= z\frac{\partial}{\partial z}(\bar{N}\ln z + Z_{C\bar{N}}) \\ &= \bar{N}\end{aligned}$$

The grand potential

$$
\begin{aligned}
\Phi_G &= -k_B T \ln Z_G \\
&\approx -k_B T \ln (z)^{\bar{N}} Z_{C\bar{N}} \\
&= -k_B T (\bar{N} \ln z + \ln Z_{C\bar{N}}) \\
&= -k_B T (\bar{N} \ln z) - k_B T \ln Z_{C\bar{N}} \\
&= F - \mu \bar{N}
\end{aligned}
$$

or

$$\Phi_G = F - \mu \bar{N}$$

where

$$F = -k_B T \ln Z_{C\bar{N}}$$

$$
\begin{aligned}
U &= \mu \langle N \rangle_G - \frac{\partial}{\partial \beta} \ln Z_G \\
&= \mu \bar{N} - \frac{\partial}{\partial \beta} (\bar{N} \ln z + \ln Z_{C\bar{N}}) \\
&= \mu \bar{N} - \frac{\partial}{\partial \beta} (\bar{N} \beta \mu) - \frac{\partial}{\partial \beta} \ln Z_{C\bar{N}} \\
&= \bar{U}
\end{aligned}
$$

We note that

$$G = \mu \bar{N} = F + PV = U - ST + PV$$

$$\Phi_G = F - \mu \bar{N} = -PV$$