Grand canonical ensemble; Overview

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In the grand canonical ensemble, the probability of the state $|E, N\rangle$ (with the energy *E* and the number of particles *N*) is given by the 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 is expressed by

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

using the grand potential $\Phi_G = -PV$.

Hew we take a brief look at the essence of the grand canonical ensemble.

1. Derivation of grand canonical ensemble

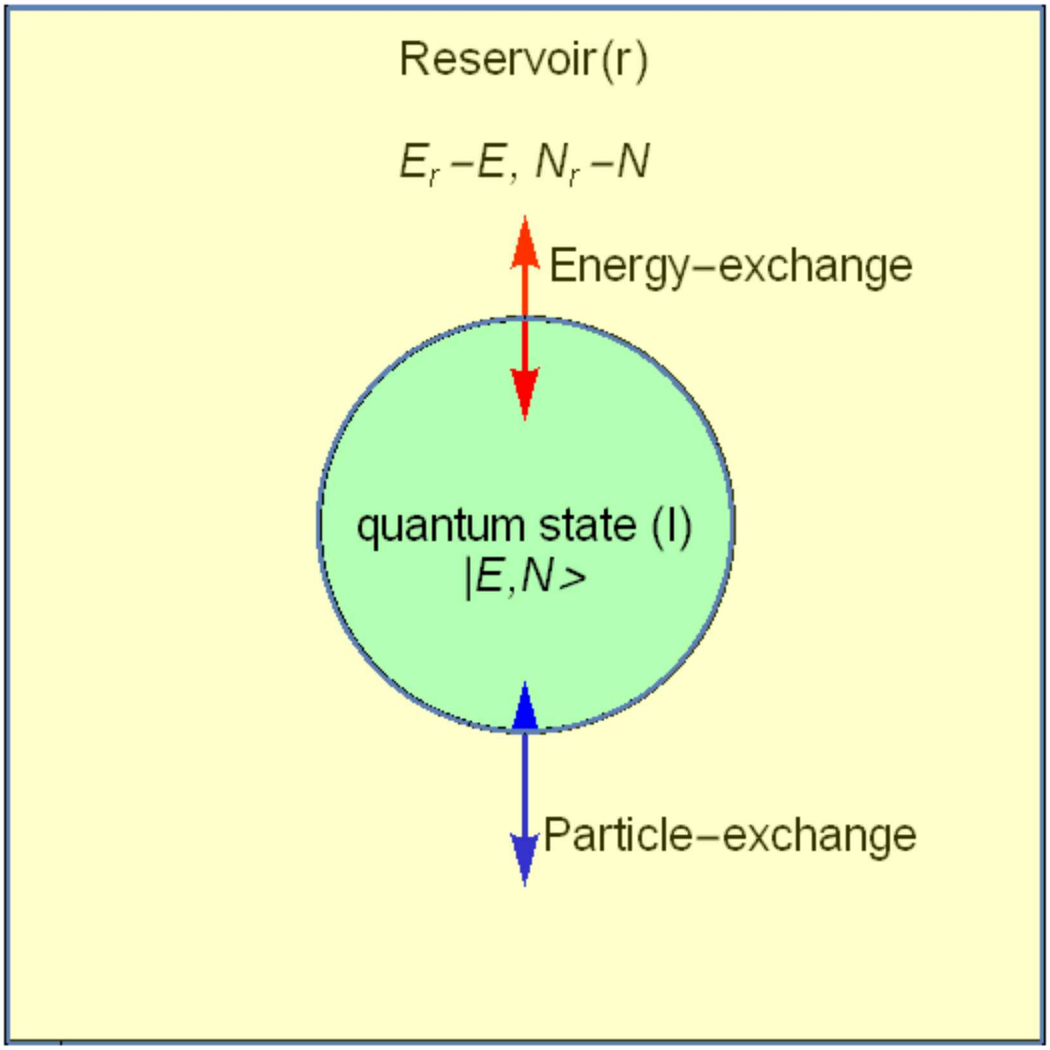

Fig. One specific state denoted by $\left|E, N\right\rangle$ (the energy E and the particle number N) surrounded by the reservoir. There are energy exchange and particle exchange between the quantum state and the reservoir.

Suppose that there is a quantum state (one state) denoted by $\left|E, N\right\rangle$ surrounded by the reservoir. The way of possible states is given by

$$W = 1 \times \Omega(E_r - E, N_r - N)$$

From the Boltzmann's principle, the entropy is expressed by

$$S = k_B \ln W = k_B \ln \Omega(E_r - E, N_r - N)$$

or

$$W = \exp(\frac{S}{k_B})$$

where k_B is the Boltzmann constant. We use the Taylor expansion,

$$\begin{aligned}
S &= k_B[\ln\Omega(E_r, N_r) - \frac{\partial \ln\Omega(E_r, N_r)}{\partial E_r} E - \frac{\partial \ln\Omega(E_r, N_r)}{\partial N_r} N \\
&= S_r - \frac{\partial S_r}{\partial E_r} E - \frac{\partial S_r}{\partial N_r} N \\
&= S_r - \frac{k_B}{k_B T} E + \frac{k_B \mu}{k_B T} N \\
&= S_r - k_B \beta E + k_B \beta \mu N
\end{aligned}$$

$$W = \exp(\frac{S}{k_B})$$

with

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN , \qquad \frac{\partial S_r}{\partial E_r} = \frac{1}{T}, \qquad \frac{\partial S_r}{\partial N_r} = -\frac{\mu}{T}$$

The probability is denoted by

$$\begin{aligned}
p(E, N) &= \exp(\frac{S_r - k_B \beta E + k_B \beta \mu N}{k_B}) \\
&= \exp(\frac{S_r}{k_B}) \exp[\beta(\mu N - E)] \\
&= \exp(\frac{S_r}{k_B}) z^N \exp(-\beta E)
\end{aligned}$$

We define the fugacity (or the absolute activity)

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

We define the grand canonical ensemble;

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

We use the partition function for the canonical ensemble, which is defined by

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

The internal energy is

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

since

$$\begin{aligned}
\frac{\partial}{\partial \beta} \ln Z_G &= \frac{1}{Z_G} \frac{\partial}{\partial \beta} Z_G \\
&= \frac{1}{Z_G} \frac{\partial}{\partial \beta} \sum_{N=0} \sum_{i(N)} z^N e^{-\beta E_i(N)} \\
&= \frac{1}{Z_G} \sum_{N=0} \sum_{i(N)} \mu N z^N e^{-\beta E_i(N)} - \frac{1}{Z_G} \frac{\partial}{\partial \beta} \sum_{N=0} \sum_{i(N)} z^N [E_i(N)] e^{-\beta E_i(N)} \\
&= \mu \langle N \rangle_G - U
\end{aligned}$$

$$\begin{aligned}
\frac{\partial}{\partial \mu} \ln Z_G &= \frac{1}{Z_G} \frac{\partial}{\partial \mu} Z_G \\
&= \frac{1}{Z_G} \frac{\partial}{\partial \mu} \sum_{N=0} \sum_{i(N)} z^N e^{-\beta E_i(N)} \\
&= \frac{1}{Z_G} \sum_{N=0} \sum_{i(N)} \beta N z^N e^{-\beta E_i(N)} \\
&= \beta \langle N \rangle_G
\end{aligned}$$

The entropy is

$$S = -k_B \sum_{N=0} \sum_{i(N)} p_i \ln p_i$$
$$= -k_B \sum_{N=0} \sum_{i(N)} p_i [N\beta\mu - \beta E_i(N) - \ln Z_G]$$
$$= -k_B \beta\mu \langle N \rangle_G + k_B \beta U + k_B \ln Z_G$$
$$= -k_B \beta\mu \langle N \rangle_G + k_B \beta\mu \langle N \rangle_G - k_B \beta \frac{\partial}{\partial \beta} \ln Z_G + k_B \ln Z_G$$
$$= k_B (\ln Z_G - \frac{\partial \ln Z_G}{\partial \ln \beta})$$

or

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

where

$$p_i = \frac{1}{Z_G} z^N \exp[-\beta E_i(N)]$$

$$\ln p_i = N \ln z - \beta E_i(N) - \ln Z_G$$
$$= N\beta\mu - \beta E_i(N) - \ln Z_G$$

The entropy S can be rewritten as

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

The average number:

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

The Helmholtz free energy

$$
\begin{aligned}
F &= U - ST \\
&= \mu \bar{N} - \frac{\partial}{\partial \beta} \ln Z_G - \frac{1}{\beta}(\ln Z_G - \beta \frac{\partial}{\partial \beta} \ln Z_G) \\
&= \mu \bar{N} - \frac{1}{\beta} \ln Z_G \\
&= \mu \bar{N} - k_B T \ln Z_G
\end{aligned}
$$

or

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

2. Grand potential: $\Phi_G = -k_B T \ln Z_G$

Here we define the grand potential Φ_G as

$$\Phi_G = -k_B T \ln Z_G \qquad \text{(Grand potential)}$$

in the grand canonical ensemble, which corresponds to the Helmholtz free energy in the canonical ensemble,

$$F_C = -k_B T \ln Z_C \qquad \text{(Canonical ensemble)}$$

Using this, we get the Helmholtz free energy as

$$F = \mu \bar{N} + \Phi_G = \mu \bar{N} - k_B T \ln Z_G$$

where we use $\bar{N} = \langle N \rangle$ for simplicity.

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

Here we show that the Gibbs free energy is expressed by

$$G = \mu \bar{N}$$

or

$$G = k_B T \frac{\partial \ln Z_G}{\partial \ln \mu}$$

The Gibbs free energy is

$$G = F + PV$$

Then we have

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

or

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

when

$$G = \mu \bar{N} .$$

3. Thermodynamic properties using $\Phi_G = -k_B T \ln Z_G = -PV$

$$\Phi_G = F - \mu \bar{N} = -k_B T \ln Z_G = -PV$$

$$\begin{aligned} d\Phi_G &= d(F - \mu \bar{N}) \\ &= -SdT - PdV + \mu d\bar{N} - \mu d\bar{N} - \bar{N} d\mu \\ &= -SdT - PdV - \bar{N} d\mu \end{aligned}$$

So we get the relations

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

We also note that

$$d(\frac{\Phi_G}{T}) = d(\frac{F-\mu\bar{N}}{T})$$
$$= d(\frac{U}{T} - S - \frac{\mu\bar{N}}{T})$$
$$= \frac{TdU - UdT}{T^2} - dS - \left(\frac{T\bar{N}d\mu + T\mu d\bar{N} - \mu\bar{N}dT}{T^2}\right)$$
$$= -\frac{UdT}{T^2} + \frac{1}{T}dU - dS + \frac{\mu\bar{N}}{T^2}dT - \frac{\bar{N}}{T}d\mu - \frac{\mu d\bar{N}}{T}$$
$$= -\frac{UdT}{T^2} + \frac{1}{T}(TdS - PdV + \mu d\bar{N}) - dS + \frac{\mu\bar{N}}{T^2}dT - \frac{\bar{N}}{T}d\mu - \frac{\mu d\bar{N}}{T}$$
$$= -\frac{(U-\mu\bar{N})}{T^2}dT - \frac{P}{T}dV - \frac{\bar{N}}{T}d\mu$$

which leads to the relation

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

leading to the result which is derived above

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

with

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

4. Average number:

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

$$\frac{\partial Z_G}{\partial z} = \sum_{N=0} N z^{N-1} Z_{CN}(\beta)$$

or

$$z\frac{1}{Z_G}\frac{\partial Z_G}{\partial z} = \frac{\partial\ln Z_G}{\partial\ln z} = \frac{1}{Z_G}\sum_{N=0} N z^N Z_{NC}(\beta) = \bar{N}$$

Note that

$$z\frac{\partial}{\partial z} = z\frac{\partial \mu}{\partial z}\frac{\partial}{\partial \mu} = z\frac{1}{\frac{\partial z}{\partial \mu}}\frac{\partial}{\partial \mu} = \frac{z}{\beta z}\frac{\partial}{\partial \mu} = k_B T\frac{\partial}{\partial \mu}$$

where $z = e^{\beta\mu}$, $\frac{\partial z}{\partial \mu} = \beta e^{\beta\mu} = \beta z$

Thus we have

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

or

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

5. Variance in the number

$$z\frac{\partial Z_G}{\partial z} = \sum_{N=0} N z^N Z_{CN}(\beta)$$

$$z\frac{\partial}{\partial z} z\frac{\partial Z_G}{\partial z} = \sum_{N=0} N^2 z^N Z_{CN}(\beta) = Z_G\langle N^2\rangle_G$$

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

Then we have

$$
\begin{aligned}
(\Delta N)^2 &= \langle N^2 \rangle_G - \langle N \rangle_G{}^2 \\
&= \frac{(k_B T)^2}{Z_G}\frac{\partial^2 Z_G}{\partial \mu^2} - (k_B T)^2 \left(\frac{1}{Z_G}\frac{\partial Z_G}{\partial \mu} \right)^2 \\
&= (k_B T)^2 [\frac{1}{Z_G}\frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G{}^2}\left(\frac{\partial Z_G}{\partial \mu} \right)^2] \\
&= (k_B T)^2 \frac{\partial}{\partial \mu}(\frac{1}{Z_G}\frac{\partial Z_G}{\partial \mu}) \\
&= (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2}
\end{aligned}
$$

Note that

$$
\frac{\partial \langle N \rangle_G}{\partial \mu} = k_B T \frac{\partial^2 \ln Z_G}{\partial \mu^2} = \frac{1}{k_B T}(\Delta N)^2
$$

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

6. Number density

We define the density *n* as

$$
n = \frac{\langle N \rangle_G}{V}, \qquad \langle N \rangle_G = nV
$$

$$
\frac{\partial n}{\partial \mu} = \frac{1}{V}\frac{\partial \langle N \rangle_G}{\partial \mu} = \frac{1}{k_B T V}(\Delta N)^2
$$

So the variance of number is given by

$$
V\frac{\partial n}{\partial \mu} = \frac{1}{k_B T}(\Delta N)^2, \quad \text{or} \qquad \frac{\partial n}{\partial \mu} = \frac{1}{k_B T V}(\Delta N)^2
$$

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

$$\Delta N = \sqrt{k_B T \frac{\partial n}{\partial \mu} V}$$

$$\frac{\Delta N}{\langle N \rangle_G} = \frac{\sqrt{k_B T \frac{\partial n}{\partial \mu} V}}{nV} = \frac{\sqrt{k_B T \frac{\partial n}{\partial \mu}}}{n} \frac{1}{\sqrt{V}}$$

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E. Fermi, Notes on Thermodynamics and Statistics (The University of Chicago, 1966).
H.S. Robertson, Statistical Thermodynamics (PRP Prentice Hall, 1993).
S.J. Blundell and K.M. Blundell, Concepts in Thermal Physics (Oxford, 2006).

APPENDIX-I Scaling relation (I): Thermodynamics

Scaling: another method of deriving the expression $G = G(T, P, N) = \mu N$
(Blundell-Blundell, Thermal Physics)

The entropy *S* is a function of *U*, *V*, and *N*. All four parameters are extensive parameters. We assume the scaling relation such that

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$$

taking into account of the extensive parameters

$$S \to \lambda S, \qquad U \to \lambda U, \qquad V \to \lambda V, \qquad N \to \lambda N$$

After differentiating this with respect to λ and subsequently setting $\lambda = 1$, we have

$$S = \frac{\partial S}{\partial U} U + \frac{\partial S}{\partial V} V + \frac{\partial S}{\partial N} N = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}$$

since

$$\frac{\partial S}{\partial U} = \frac{1}{T} \qquad \frac{\partial S}{\partial V} = \frac{P}{T}, \qquad \frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

Thus we have the relation

$$U - ST + PV = \mu N, \qquad F = U - ST$$

leading to

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

((**Note**))

$$dU = TdS - PdV + \mu dN$$

$$F = U - ST$$

$$\begin{aligned} dF &= dU - SdT - TdS \\ &= TdS - PdV + \mu dN - SdT - TdS \\ &= -SdT - PdV + \mu dN \end{aligned}$$

and

$$G = F + PV$$

$$\begin{aligned} dG &= dF + PdV + VdP \\ &= -SdT - PdV + \mu dN + PdV + VdP \\ &= -SdT + VdP + \mu dN \end{aligned}$$

APPENDIX-II Scaling relation (II): Thermodynamics

Here we show that

$$G = G(T, P, N) = \mu N$$

Note that the Gibbs free energy is a function of *T*, *P*, and *N*. The variables (*T* and *P*) are intensive parameter, while *N* is the extensive parameter. Since *G* is the extensive quantity, we can assume the scaling relation,

$$G(T, P, \lambda N) = \lambda G(T, P, N)$$

where λ is arbitrary. We take the derivative of the above equation with respect to λ and after that we choose λ =1.

$$N\left(\frac{\partial G(T,P,N)}{\partial N}\right)_{T,P} = G(T,P,N)$$

Then we have

$$G = G(T,P,N) = \mu N$$

since

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