From canonical ensemble to grand canonical ensemble: relation

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Here we discuss the relation between the thermodynamic properties in the canonical ensemble and grand canonical ensemble. We need to make it clear how the Helmholtz free energy defined in the canonical ensemble is redefined in the grand canonical ensemble. The partition function of the grand canonical ensemble is related to that of the canonical ensemble as

$$Z_G(z) = z^{\bar{N}} Z_C(\bar{N}, \beta)$$

with $\bar{N} = \langle N \rangle_G$.

1. Helmholtz free energy in the Grand canonical ensemble

We start with the thermodynamic relation (see the Appendix)

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

where G is the Gibbs free energy. F is the Helmholtz free energy,

$$F = -k_B T \ln Z_C(N, \beta) \qquad \text{(Canonical ensemble)}$$

In the grand canonical ensemble, N has a sharp peak at $N = \bar{N}$, so the Helmholtz free energy can be rewritten as

$$F = -k_B T \ln Z_C(\bar{N}, \beta)$$

where $\bar{N}$ is the average number in the grand canonical ensemble and is defined by

$$\bar{N} = z\frac{\partial}{\partial z}\ln Z_G(z) = \frac{\partial}{\partial \ln z}\ln Z_G(z) = \frac{\partial}{\partial(\beta\mu)}\ln Z_G(z) \qquad \text{(Grand canonical)}$$

We note that the grand canonical ensemble partition function is defined by

$$Z_G(z) = \sum_N z^N Z_C(N, \beta).$$

Using the Cauchy theorem in the complex plane (see the textbook of Arfken), $Z_C(N,\beta)$ can be written as

$$Z_C(N,\beta) = \frac{1}{2\pi i}\oint \frac{Z_G(z)}{z^{N+1}}dz = \frac{1}{2\pi i}\oint \frac{Z_G(z)}{z^N}\frac{dz}{z}$$

We note that

$$f(z) = \frac{Z_G(z)}{z^N} = \exp[\ln Z_G(z) - N\ln z]$$

Suppose that $f(z)$ has a sharp peak at $z = z^*$. Using the Taylor expansion, thus we have

$$f(z) = f(z^*) + (z - z^*)f'(z^*) + ...$$

with $f'(z^*) = 0$. In other words, we get

$$f'(z^*) = \exp[\ln Z_G(z^*) - N\ln z^*][\frac{\partial}{\partial z^*}\ln Z_G(z^*) - \frac{N}{z^*}] = 0$$

or

$$z^*\frac{\partial}{\partial z^*}\ln Z_G(z^*) = N$$

or

$$\frac{\partial}{\partial z^*}\ln Z_G(z^*) = \frac{N}{z^*}$$

or

$$N = \frac{\partial}{\partial \ln z^*}\ln Z_G(z^*) \qquad \text{(Canonical ensemble)} \qquad (1)$$

Thus we get

$$f(z) = f(z^*)$$

and

$$\begin{aligned} Z_C(N,\beta) &= \frac{1}{2\pi i}\oint f(z*)\frac{dz}{z} \\ &= f(z^*) \\ &= \exp[\ln Z_G(z^*) - N\ln z^*] \\ &= (z^*)^{-N} Z_G(z^*) \end{aligned}$$

or

$$Z_C(N,\beta) = (z^*)^{-N} Z_G(z^*)$$

From the definition of the average number in the grand canonical ensemble

$$\bar{N} = \frac{\partial}{\partial(\beta\mu)}\ln Z_G(z) = \frac{\partial}{\partial \ln z}\ln Z_G(z) \qquad \text{(Grand canonical)} \qquad (2)$$

The comparison between Eq.(1) and Eq.(2) leads to the correspondence between the canonical ensemble and the grand canonical ensemble,

$$N \to \bar{N} = \langle N \rangle_G$$

$$z^* \to z$$

Finally, we get the expression

$$Z_C(\bar{N},\beta) = (z)^{-\bar{N}} Z_G(z) = \exp[-\bar{N}\ln z + \ln Z_G(z)]$$

This is the relation of the partition function in the canonical ensemble and grand canonical ensemble.

Using the above relation, we can evaluate the Helmholtz free energy;

$$\begin{aligned} F &= -k_B T \ln Z_C(\bar{N},\beta) \\ &= -k_B T[-\bar{N}\ln z + \ln Z_G(z)] \\ &= -k_B T \ln Z_G(z) + \mu\bar{N} \end{aligned}$$

since $\ln z = \beta\mu$. We introduce the grand potential as

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

or

$$PV = k_B T \ln Z_G(z)$$

where

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

2. Summary

The above discussion is summarized as follows.

$$F = -k_B T \ln Z_C(\bar{N}, \beta) = -k_B T \ln Z_G(z) + \mu\bar{N}$$

where

$$\bar{N} = \frac{\partial}{\partial \ln z} \ln Z_G(z)$$

and

$$Z_C(\bar{N}, \beta) = \exp[-\bar{N} \ln z + \ln Z_G(z)]$$

Thermodynamic relation:

$$\Phi_G = -PV = F - \mu\bar{N} = F - G = -k_B T \ln Z_G(z),$$

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