Grand canonical ensemble: Scaling relation of thermodynamic properties

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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Suppose that there are λ systems which have the same variables of state (in other words, the same state). We now combine these systems into one whole system by contacting together. Before the contact, all the systems are in thermal equilibrium. After the contact, there occurs no change in the system. The combined system is also in thermal equilibrium. There are two types of variables: intensive variables and extensive variables.

$$U \to \lambda U \qquad \text{(extensive)}$$
$$S \to \lambda S \qquad \text{(extensive)}$$
$$V \to \lambda V \qquad \text{(extensive)}$$
$$N \to \lambda N \qquad \text{(extensive)}$$
$$P \to P \qquad \text{(intensive)}$$
$$T \to T \qquad \text{(intensive)}$$

1. Scaling relation of Gibbs free energy

We show that

$$G = \mu N$$

We note the scaling relation of the Gibbs free energy

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

Taking a derivative of both sides with respect to λ and putting $\lambda = 1$, we get

$$N[\frac{\partial G(T,P,N)}{\partial N}]_{T,P} = G(T,P,N)$$

or

$$N[\frac{\partial G(T,P,N)}{\partial N}]_{T,P} = G(T,P,N)$$

where

$$dG = -SdT + VdP + \mu dN$$

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

2. Scaling relation of entropy

(Blundell and Blundell)

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

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

where

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

$$S = \frac{\partial S}{\partial(\lambda U)}\frac{\partial(\lambda U)}{\partial \lambda} + \frac{\partial S}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial S}{\partial(\lambda N)}\frac{\partial(\lambda N)}{\partial \lambda}$$

or

$$\begin{aligned} S &= \frac{\partial S}{\partial U}U + \frac{\partial S}{\partial V}V + \frac{\partial S}{\partial N}N \\ &= \frac{1}{T}U + \frac{PV}{T} - \frac{\mu N}{T} \end{aligned}$$

or

$$U - ST = -PV + \mu N$$

We note that

$$F = U - ST\,, \qquad G = F + PV$$

Thus we have

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

where

$$dU = TdS - PdV + \mu dN, \qquad dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

3. Scaling relation of Helmholtz free energy

$$F = F(N, V, T)$$

$$\lambda F = F(\lambda N, \lambda V, T)$$

We take a derivative of the above equation with respect to l and then put $\lambda = 1$.

$$F = \frac{\partial F}{\partial(\lambda N)}\frac{\partial(\lambda N)}{\partial\lambda} + \frac{\partial F}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial\lambda}$$

or

$$\begin{aligned} F &= \frac{\partial F}{\partial N}N + \frac{\partial F}{\partial V}V \\ &= \mu N - PV \end{aligned}$$

or

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

We note that

$$F = U - ST, \qquad G = F + PV$$

Thus we have

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

where

$$dF = d(U - ST) = -SdT - PdV + \mu dN$$

4. Gibbs-Duhem relation

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

Since $G = \mu N$, we have

$$\mu dN + Nd\mu = -SdT + VdP + \mu dN$$

Finally, we get the Gibbs-Duhem relation

$$Nd\mu + SdT - VdP = 0 .$$