Top Ten Items

Chapters 1-3

1. Thermodynamic State Functions

Legendre Transform (Ch.1, p.15-p.17):

$$y = \phi + Px \;\rightarrow\; \phi = y - Px \quad \boxed{y = y(x) \rightarrow \quad \phi = \phi(P)}$$

From the 1st law of thermodynamics (*dE=TdS-pdV*: for one component system), we have $y = E$ and two slopes available: $\left(\dfrac{\partial E}{\partial S}\right)_V = T, \quad \left(\dfrac{\partial E}{\partial V}\right)_S = -p$

Ex 1. Helmholtz free energy

Seek a function whose natural variables are T and *V*.: Since *E=E(S,V)*, we need to replace only *S* with *T*. So Look for the slope that gives *T* in the above. That is $\left(\partial E/\partial S\right)_V = T$, therefore we set $y = E, \quad x = S, \quad P = -p$ to get $\phi = E - TS$.

Ex 2. Enthalpy

Seek a function whose natural variables are S and *p*. In this case we need to replace only *V* with *p*. So use the slope $P = \left(\partial E/\partial V\right)_S = -p, \quad$ then $V \rightarrow x$.

Therefore the function you wanted is: $\phi = y - Px = \boxed{E + pV = H(S, p)}$ called Entalphy.

Ex 3. Gibb's free energy

Seek a function whose natural variables are T and *p*. In this case, we need to replace both *(S,V)* with *(T, p)*. The Legendre Transformation can be extended to:

$$\phi = y - Px \quad \mapsto \quad \phi = y - \sum_j P_j x_j$$

Choose $P_1 = \left(\dfrac{\partial E}{\partial S}\right)_V = T, \quad P_2 = \left(\dfrac{\partial E}{\partial V}\right)_S = -p, \quad$ then $S \rightarrow x_1, \quad V \rightarrow x_2$

$$\phi = y - P_1 x_1 - P_2 x_2 = E - TS - (-p)V = \boxed{E - TS + pV \equiv G(T, p)},$$ Gibb's free energy.

Ex 4. Chemical potential in multi-component systems

In general E,A,H, and G depend on the number of moles or molecules of each component. Nj = the number of moles of component j and μj = chemical potential of component j.

$$dE = TdS - pdV + \sum_j \left(\frac{\partial E}{\partial N_j}\right)_{S,V,N_{k\neq j}} dN_j = TdS - pdV + \sum_j \mu_j dN_j$$

$$dH = TdS + Vdp + \sum_j \mu_j dN_j, \quad dA = -SdT - pdV + \sum_j \mu_j dN_j, \quad dG = -SdT + Vdp + \sum_j \mu_j dN_j$$

These equations show that $\boxed{\mu_j = \left(\frac{\partial E}{\partial N_j}\right)_{S,V,\ldots} = \left(\frac{\partial H}{\partial N_j}\right)_{S,p,\ldots} = \left(\frac{\partial A}{\partial N_j}\right)_{V,T,\ldots} = \left(\frac{\partial G}{\partial N_j}\right)_{p,T,\ldots}}$

2. Determination of the Grand Canonical Partition Function, Q

Use Lagrangian undetermined parameter method. For any possible distribution number of states, maximize $W\left(\{a_{Nj}\}\right) = \dfrac{A!}{\prod_N \prod_j a_{Nj}!}$ or its logarithm under

constraints: $\sum_N \sum_j a_{Nj} = A, \quad \sum_N \sum_j a_{Nj} E_{Nj} = \mathrm{E}, \quad \sum_N \sum_j a_{Nj} N = \mathrm{N}.$

We thus formulate as:

$$\frac{\partial}{\partial a_{Nj}}\left[\ln W\left(\{a_{Nj}\}\right) - \alpha \sum_N \sum_j a_{Nj} - \beta \sum_N \sum_j a_{Nj} E_{Nj} - \gamma \sum_N \sum_j a_{Nj} N\right]_{a_{Nj}=a_{Nj}^*} = 0$$

$$\rightarrow \quad a_{Nj}^* = e^{-\alpha} e^{-\beta E_N j(V) - \gamma N}$$

$$P_{N j}(V,\beta,\gamma) = \frac{a_{Nj}^*}{A} = \frac{e^{-\beta E_N j(V) - \gamma N}}{\sum_N \sum_j e^{-\beta E_N j(V) - \gamma N}} = \frac{e^{-\beta E_N j(V) - \gamma N}}{Z}$$

$$\overline{E}(V,\beta,\gamma) = \frac{1}{Z}\sum_N \sum_j E_{Nj}(V) e^{-\beta E_N j(V) - \gamma N} = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,\gamma}$$

$$\overline{p}(V,\beta,\gamma) = \frac{1}{Z}\sum_N \sum_j \left(-\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_N j(V) - \gamma N} = \left(\frac{\partial \ln Z}{\partial V}\right)_{\beta,\gamma}$$

$$\overline{N}(V,\beta,\gamma) = \frac{1}{Z}\sum_N \sum_j N\, e^{-\beta E_N j(V) - \gamma N} = -\left(\frac{\partial \ln Z}{\partial \gamma}\right)_{V,\beta}$$

Now proceed with

$$\left(\frac{\partial \overline{E}}{\partial V}\right)_{\gamma,\beta} = \frac{\sum_{N,j}\left(\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_{Nj} - \gamma N}}{Z} - \beta \frac{\sum_{N,j} E_{Nj}\left(\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_{Nj} - \gamma N}}{Z} + \beta \frac{\left\{\sum_{N,j} E_{Nj} e^{-\beta E_{Nj} - \gamma N}\right\}\left\{\sum_{N,j}\left(\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_{Nj} - \gamma N}\right\}}{Z^2}$$

$$= -\overline{p} + \beta \overline{Ep} - \beta \overline{E}\,\overline{p}$$

Similary, $\left(\frac{\partial \overline{p}}{\partial \beta}\right)_{\gamma,V} = \overline{E}\,\overline{p} - \overline{EP}$, therefore $\left(\frac{\partial \overline{E}}{\partial V}\right)_{\gamma,\beta} + \beta\left(\frac{\partial \overline{p}}{\partial \beta}\right)_{\gamma,V} = -\overline{p}$

By comparison with the thermodynamic relation (Pr. 1-29), and with assumption: $\overline{E} \leftrightarrow E,\ \overline{p} \leftrightarrow p$

we find $\boxed{\beta = \frac{1}{T} \times \text{const} \equiv \frac{1}{kT}}$, although we still don't know about γ at the moment.

3. Alternative determination of β, γ that leads to the relationship between Entropy and Partition Functions

For Grand Canonical Ensemble Z,

$$f = \ln Z \quad \text{or} \quad f(\beta, \gamma, \{E_{N,j}(V)\}) = \ln\left\{\sum_N \sum_j e^{-\beta E_{Nj}(V) - \gamma N}\right\}$$

Total derivative of f

$$df = \left(\frac{\partial f}{\partial \beta}\right)_{\gamma,E} d\beta + \left(\frac{\partial f}{\partial \gamma}\right)_{\beta,E} d\gamma + \sum_N \sum_j \left(\frac{\partial f}{\partial E_{Nj}}\right) dE_{Nj} = -\bar{E} d\beta - \bar{N} d\gamma - \beta \sum_N \sum_j P_{Nj} dE_{Nj}$$

The last term represents an ensemble average of reversible work done by the system, so

$df + \bar{E} d\beta + \bar{N} d\gamma = -\beta \sum_N \sum_j P_{Nj} dE_{Nj} = +\beta \bar{p} dV$ Add to both sides, $\beta d\bar{E} + \gamma d\bar{N}$

$$d(f + \beta \bar{E} + \gamma \bar{N}) = \beta d\bar{E} + \gamma d\bar{N} + \beta \bar{p} dV$$

Now compare this with $TdS = dE + pdV - \mu dN$ or identifying

$$dS = d(f + \beta \bar{E} + \gamma \bar{N}) \quad and \quad \frac{dE}{T} + \frac{pdV}{T} - \frac{\mu dN}{T} = \beta d\bar{E} + \gamma d\bar{N} + \beta \bar{p} dV$$

$$\therefore \quad \beta = \frac{1}{T} \times \text{const} \equiv \frac{1}{kT} \quad \gamma = -\frac{\mu}{T} \times \text{const} \equiv -\frac{\mu}{kT}$$

BTW we also found a relation between Z and S:

$$\boxed{S = f + \beta \bar{E} + \gamma \bar{N} = \frac{\bar{E}}{T} - \frac{\bar{N}\mu}{T} + k \ln Z}$$

For Canonical Ensemble Q,

Similarly, we could relate S to Q, if we used in the above $f = \ln Q$ instead of $f = \ln Z$:

$$f = \ln Q \quad or \quad f(\beta, E_1, E_2, ...) = \ln\left\{\sum_j e^{-\beta E_j}\right\}$$

$$df = \left(\frac{\partial f}{\partial \beta}\right) d\beta + \sum_k \left(\frac{\partial f}{\partial E_k}\right) dE_k = -\frac{\sum_j E_j e^{-\beta E_j}}{Q} d\beta - \sum_k \frac{\beta e^{-\beta E_k}}{Q} dE_k = -\bar{E}\, d\beta - \beta \sum_k P_k\, dE_k$$

To compare $d(f + \beta \bar{E}) = \beta(d\bar{E} - \sum_k P_k\, dE_k)$ with $dS = \frac{1}{T}(dE + pdV)$, we get $\beta = \frac{1}{kT}$

and $\quad d(f + \beta E) = \beta d(TS), \ln Q + \beta \bar{E} = \beta TS + \text{constant}, \ln Q + \frac{\bar{E}}{kT} = \frac{S}{k} + \text{constant}$

$$\boxed{S = k \ln Q + \frac{\bar{E}}{kT} = k \ln Q + kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}}$$

4. Proof of S = k ln Ω

i) Using Grand Canonical Ensemble

$$S_e = AS$$

$$S = k(\beta \bar{E} + \gamma \bar{N} + \ln Z)$$

$$= k \ln Z + k \sum_{N,j} (\beta E_{N,j} + \gamma N) \frac{e^{-\beta E_{N,j} - \gamma N}}{Z} = k \ln Z - k \sum_{N,j} (\ln a^*_{N,j} + \ln Z - \ln A) \frac{a^*_{N,j}}{A}$$

where we used:

$$a^*_{N,j} = \frac{A e^{-\beta E_{N,j} - \gamma N}}{Z} \quad \text{and} \quad \beta E_{N,j} + \gamma N = -\ln\left(\frac{a^*_{N,j}}{A} Z \right)$$

Note: $\sum_{N,j} \frac{a^*_{N,j}}{A} = 1$, therefore

$$S = k \ln Z - \frac{k}{A} \sum_{N,j} a^*_{N,j} \ln a^*_{N,j} - k \ln Z + k \ln A = \frac{k}{A}\left(A \ln A - \sum_{N,j} a^*_{N,j} \ln a^*_{N,j} \right)$$

$$S_e = AS = k\left(A \ln A - \sum_{N,j} a^*_{N,j} \ln a^*_{N,j} \right) = k \ln W\left(\left\{ a^*_{N,j} \right\} \right)$$

Since W is the number of states available to the system, $W = \Omega$.

$$S_e = k \ln \Omega(N, V, E)$$

ii) Using Canonical Ensemble

$$S = k \ln Q + \frac{\bar{E}}{T} = k \ln Q + \frac{1}{T} \sum_j \frac{E_j e^{-\beta E_j}}{Q}$$

Since $a^*_j = e^{-\alpha - \beta E_j} = \frac{A}{Q} e^{-\beta E_j}$, we may use $\frac{e^{-\beta E_j}}{Q} = \frac{a^*_j}{A}$, $\beta E_j = -\ln \frac{Q}{A} a^*_j$.

$$S = k \ln Q + k \sum_j \left[\ln A - \ln Q - \ln a^*_j \right] \frac{a^*_j}{A} = k \ln Q - k \ln A - k \ln Q - \sum_{N,j} \frac{a^*_j \ln a^*_j}{A}$$

$$= \frac{k}{A}\left[(A \ln A - A) - \left(\sum_j a^*_j \ln a^*_j - \sum_j a^*_j \right) \right] \approx \frac{k}{A} \ln\left(\frac{A!}{a^*_j !} \right)$$

$$S_e = AS = k \ln \Omega(N, V, E)$$

5. Proof of A = - kT ln Q

Given $Q = Q(V, N, T) = \sum_j e^{-E_j(N,V)/kT}$

We have $\bar{E} = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$, $S = \frac{\bar{E}}{T} + k \ln Q = kT \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q$

$$A = E - TS = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} - T\left[kT \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k \ln Q\right] = -kT \ln Q$$

6. Proof of pV = kT ln Z

Method 1: use $G = \mu N$

$$G = E + pV - TS = E + pV - T\left(\frac{\bar{E}}{T} - \frac{\bar{N}\mu}{T} + k \ln Z\right) = pV + \mu \bar{N} - kT \ln Z$$

$N \leftrightarrow \bar{N}$ gives $\boxed{pV = kT \ln Z}$

Method 2: use Euler's theorem. To see if $f = \ln Z$ is a homogeneous function of V, recall

$df = \left(\frac{\partial f}{\partial \beta}\right)_{\gamma,E} d\beta + \left(\frac{\partial f}{\partial \gamma}\right)_{\beta,E} d\gamma + \sum_N \sum_j \left(\frac{\partial f}{\partial E_{Nj}}\right) dE_{Nj} = -\bar{E} d\beta - \bar{N} d\gamma + \beta p dV$. Now fixing T, μ,

$df\big|_{\beta,\gamma} = \beta p dV$ therefore f is a homogeneous function of V of order 1, in which case

$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{1}{\beta}\frac{\ln Z}{V}$ or $\boxed{pV = kT \ln Z}$

7. Proof of G = kT ln Δ

$f = \ln Z$ or $f(\beta, \gamma, \{E_{N,j}(V)\}) = \ln\left\{\sum_N \sum_j e^{-\beta E_{Nj}(V) - \gamma V}\right\}$

Total derivative of f

$df = \left(\frac{\partial f}{\partial \beta}\right)_{\gamma,E} d\beta + \left(\frac{\partial f}{\partial \gamma}\right)_{\beta,E} d\gamma = -\bar{E} d\beta - \bar{V} d\gamma$. Adding to both sides $\beta d\bar{E} + \gamma d\bar{V}$,

$d(f + \beta \bar{E} + \gamma \bar{V}) = \beta d\bar{E} + \gamma d\bar{V}$, Now compare this with $TdS = dE + pdV$

$dS = d(f + \beta \bar{E} + \gamma \bar{V})$ *and* $\frac{dE}{T} + \frac{pdV}{T} = \beta d\bar{E} + \gamma d\bar{V}$

$\therefore \quad \beta = \frac{1}{T} \times \text{const} \equiv \frac{1}{kT} \quad \gamma = \frac{p}{T} \times \text{const} \equiv \frac{p}{kT}$, Also $S = f + \beta \bar{E} + \gamma \bar{V} = \ln \Delta + \frac{\bar{E}}{T} - \frac{p\bar{V}}{T}$

$\therefore \boxed{\ln \Delta = \frac{TS - \bar{E} + p\bar{V}}{T} = \frac{G}{T}}$

8. Thermodynamic connections in various types of ensemble

Table 3-1

$$S = k\ln\Omega(N,V,E) \quad \to dS = \frac{dE + pdV - \mu dN}{T} \to \frac{1}{T} = k\left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N}, \frac{p}{T}, \frac{\mu}{T}$$

$$A = -kT\ln Q(N,V,T) \quad \to dA = -SdT - pdV + \mu dN \quad \to S, p, \mu,\ E$$

$$pV = kT\ln Z(V,T,\mu) \quad \to d(pV) = SdT + Nd\mu + pdV \to S, N, p$$

$$G = -kT\ln\Delta(N,T,p) \quad \to dG = -SdT + Vdp + \mu dN \quad \to S, V, \mu$$

Note which set of variables is fixed in each ensemble, and which variables are derived from the logarithm of the partition function. Note also that *S* is never fixed-if it were, nothing else would happen.

9. Relationship between Ω and Q

The fluctuation theory shows that fluctuation is small in a system of large *N*. Therefore

$$Q(N,V,T) = \sum_j e^{-E_j/kT} = \sum_E \Omega(N,V,E)e^{-E/kT} \approx \Omega(N,V,\bar{E})e^{-\bar{E}/kT}$$

Suppose we did not know $A = -k\ln Q$ but know $\boxed{S = k\ln\Omega}$

$$S = k\ln\Omega = k\left[\ln Q + \frac{\bar{E}}{kT}\right] \quad \text{or} \quad \ln Q = \frac{S}{k} - \frac{\bar{E}}{kT} = \frac{TS - \bar{E}}{kT} = -\frac{A}{kT}$$

We thus recovered the relation: $A = kT\ln Q$ from $S = k\ln\Omega$.

10. An Example of Ω

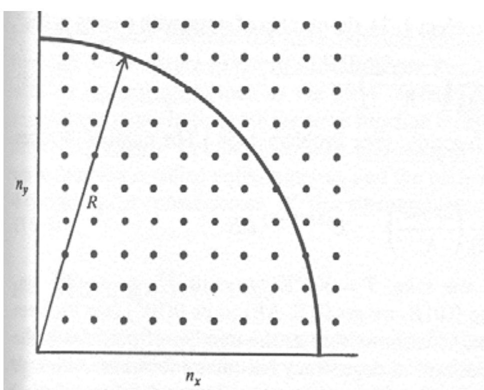

Figure 1-1. A two-dimensional version of the (n_x, n_y, n_z) space

The above shown relation $S = k\ln\Omega$ is the best known equation in statistical thermodynamics. It says: the more states available to a system, the higher the entropy is. Boltzmann is the first person to see how probability ideas could be combined with mechanics. But his idea was not well accepted at his time. Do we know what Ω looks like? Yes, in Chapter 1, we have shown that for an *N*-particle system:

$$E = \frac{h^2}{8ma^2}\sum_{j=1}^{N}(n_{xj}{}^2 + n_{yj}{}^2 + n_{zj}{}^2)$$

Using the volume of N-dim sphere, the number of states with energy ≤ E is found

$$\Omega(E) = \frac{1}{\Gamma(N+1)\Gamma(3N/2)}\left(\frac{2\pi ma^2}{h^2}\right)^{3N/2} E^{3N/2-1}$$

Keep terms of order O(N) only,

$$\ln\Gamma(N+1) \approx N\ln N - N = N\ln\left(\frac{N}{e}\right)$$

$$\ln\Gamma(3N/2) \approx \left(\frac{3N}{2}-1\right)\ln\left(\frac{3N}{2}-1\right) - \left(\frac{3N}{2}-1\right) \approx \left(\frac{3N}{2}\right)\ln\left(\frac{3N}{2e}\right)$$

$$\ln\left(\frac{2\pi ma^2}{h^2}\right)^{3N/2} = N\ln\left(\frac{2\pi ma^2}{h^2}\right)^{3/2} = N\ln\left(\frac{2\pi m}{h^2}\right)^{3/2} V$$

$$\ln E^{3N/2-1} = N\left(\ln E^{3/2} - \frac{1}{N}\ln E\right) \approx N\ln E^{3/2} \approx N\ln\left(\frac{3}{2}NkT\right)^{3/2}$$

Put them back,

$$\ln\Omega \approx N\ln\left[\left(\frac{N}{e}\right)^{-1}\right]\left[\left(\frac{3N}{2e}\right)^{-3/2}\right]\left[\left(\frac{2\pi m}{h^2}\right)^{3/2} V\right]\left[\left(\frac{3}{2}NkT\right)^{3/2}\right]$$

$$\therefore \quad \boxed{\Omega \approx \left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right]^N}$$

Check up using $p = T\left(\frac{\partial S}{\partial V}\right)_{E,N}$:

$$S = k\ln\Omega(N,V,E) = Nk\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right]$$

$$p = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = T\frac{\partial}{\partial V}\left[Nk\ln\left\{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{Ve^{5/2}}{N}\right\}\right] \quad \text{or} \quad pV = NkT$$