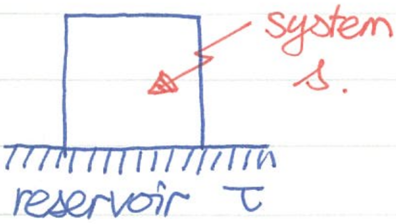
HH0061 Helmholtz Free Energy.

Introduce the Helmholtz free energy $\boxed{F \equiv U - \tau\sigma}$



For a system in thermal equilibrium with a reservoir, its Helmholtz free energy is a minimum.

$$dF_s = dU_s - \tau_s d\sigma_s - \cancel{\sigma_s d\tau_s} = dU_s - \tau d\sigma_s$$

extremum

Because $(\partial\sigma_s/\partial U_s)_{N,V} = 1/\tau$, $dU_s = \tau d\sigma_s$. Thus, $\boxed{dF_s = 0}$

Now we want to show that it's indeed a minimum.

$$\sigma = \sigma_R + \sigma_s = \sigma_R(U_0 - U_s) + \sigma_s(U_s) \cong \sigma_R(U_0) - \frac{\partial\sigma_R}{\partial U_R} U_s + \sigma_s$$

Recall the definition of temperature, $\partial\sigma_R/\partial U_R = 1/\tau$

$$\sigma = \sigma_R(U_0) - \frac{1}{\tau} U_s + \sigma_s = \sigma_R(U_0) - F_s/\tau$$

Thermal equilibrium maximizes the total entropy σ $\rightarrow$ minimize the Helmholtz free energy of the system s.

⊘ Relation between F and Z.

It's quite interesting that the Helmholtz free energy F and the partition function Z are related, $\boxed{F = -\tau \log Z}$ simple relation ☺

Here is the proof —

At temperature τ, the probability distribution is Boltzmann,

$P_s = \frac{1}{Z} e^{-\varepsilon_s/\tau}$. The entropy of the system is $\sigma = \langle -\log P_s \rangle$

$$\rightarrow \sigma = \left\langle \log Z + \frac{\varepsilon_s}{\tau} \right\rangle = \log Z + \frac{1}{\tau}\langle \varepsilon_s \rangle$$

just U ☺

Rewriting the above relation $\tau\sigma = \tau \log Z + U$

It's quite easy to see that $-\tau \log Z = U - \tau\sigma = F$ ☺

⓪ Differential relation for F.

$dF = \underbrace{dU - \tau d\sigma} - \sigma d\tau$, 1^{st} law $\tau d\sigma = dU - p dV$.

$\rightarrow \quad dF = -\sigma d\tau - p dV = \left(\frac{\partial F}{\partial \tau}\right)_V d\tau + \left(\frac{\partial F}{\partial V}\right)_\tau dV$

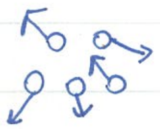
Thus, we obtain the useful relations,

$\boxed{\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma}$ and $\boxed{\left(\frac{\partial F}{\partial V}\right)_\tau = -p}$ ← It gives us a different way to understand p.

$p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \underbrace{-\left(\frac{\partial U}{\partial V}\right)_\tau + \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau}$

1^{st} term: energy pressure
2^{nd} term: entropy pressure

 solids: $-\left(\frac{\partial U}{\partial V}\right)_\tau$ dominates.

 gases: $\tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau$ dominates.

Take ideal gas as an example — $U = \frac{3}{2}N\tau$

$\left(\frac{\partial U}{\partial V}\right)_\tau = 0$, The pressure is from the entropy changes. Later, we will learn that One can compute the pressure for the ideal gas,

$\underbrace{\sigma = N\left[\log\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]}$

Sackur-Tetrode equation.

$p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \tau\left(\frac{\partial \sigma}{\partial V}\right)_\tau = \tau \cdot \frac{\partial}{\partial V}\left[N\log V + \text{other terms}\right]$

$\rightarrow \quad \underbrace{p = \tau \cdot \frac{N}{V}}$ This is just the well-known ideal-gas law.

These relations can also be understood by Legendre transform.

entropy $\sigma = \log g(U,V) = \sigma(U,V)$ OR $U = U(\sigma, V)$

Perform Legendre transform for the variable σ to τ.

$\tau = \left(\frac{\partial U}{\partial \sigma}\right)_V$ and the free energy $F = F(\tau, V) = U - \tau\sigma$

$dF = \left(\frac{\partial F}{\partial \tau}\right)_V d\tau + \left(\frac{\partial F}{\partial V}\right) dV = \cancel{\left(\frac{\partial U}{\partial \sigma}\right)_V d\sigma} + \left(\frac{\partial U}{\partial V}\right)_\sigma dV - \cancel{\tau d\sigma} - \sigma d\tau$

By comparison, $\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$ and $\left(\frac{\partial F}{\partial V}\right)_\tau = \left(\frac{\partial U}{\partial V}\right)_\sigma = -p$.

This is the same story between $L(q,\dot{q})$ and $H(q,p) \equiv p\dot{q} - L$

$$p \equiv \frac{\partial L}{\partial \dot{q}} \longleftrightarrow \dot{q} = \frac{\partial H}{\partial p} \quad \text{and} \quad dH = \dot{q}\,dp + p\,d\dot{q} - dL$$

$$\Rightarrow dH = \dot{q}\,dp + \cancel{p\,d\dot{q}} - \frac{\partial L}{\partial q}dq - \cancel{\frac{\partial L}{\partial \dot{q}}d\dot{q}} = \frac{\partial H}{\partial q}dq + \frac{\partial H}{\partial p}dp$$

$$\frac{\partial H}{\partial p} = \dot{q} \quad \text{and} \quad \frac{\partial H}{\partial q} = -\frac{\partial L}{\partial q} = -\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) = -\dot{p}$$

⓪ Free energy for binary model.

$\uparrow\uparrow\downarrow\downarrow$ $\quad N_\uparrow = \frac{N}{2} + s$

$\uparrow\uparrow\uparrow\downarrow$ $\quad N_\downarrow = \frac{N}{2} - s$

$\downarrow\downarrow\uparrow\uparrow$

The multiplicity is $g = N!/N_\uparrow!\,N_\downarrow!$

$$\sigma = \log g = \log N! - \log N_\uparrow! - \log N_\downarrow!$$

$$\approx N\log N - \cancel{N} - N_\uparrow \log N_\uparrow + \cancel{N_\uparrow} - N_\downarrow \log N_\downarrow + \cancel{N_\downarrow}$$

$$\Rightarrow \quad \sigma \cong -N_\uparrow \log\left(\frac{N_\uparrow}{N}\right) - N_\downarrow \log\left(\frac{N_\downarrow}{N}\right)$$

$$= -\left(\tfrac{1}{2}N + s\right)\log\left(\tfrac{1}{2} + \tfrac{s}{N}\right) - \left(\tfrac{1}{2}N - s\right)\log\left(\tfrac{1}{2} - \tfrac{s}{N}\right)$$

The Landau free energy is

$$\boxed{F_L(\tau, s) \equiv U(s) - \tau\sigma(s) = -2smB - \tau\sigma(s)}$$

Minimize $F_L(\tau,s)$ to get the Helmholtz free energy.

$$\frac{\partial F_L}{\partial s} = 0 \Rightarrow -2mB + \tau\log\left(\tfrac{1}{2} + \tfrac{s}{N}\right) + \tau\left(\cancel{\tfrac{1}{2}N + s}\right)\cdot\frac{1}{\cancel{\left(\tfrac{1}{2} + \tfrac{s}{N}\right)}}^{N}$$

$$- \tau\log\left(\tfrac{1}{2} - \tfrac{s}{N}\right) - \tau\left(\cancel{\tfrac{1}{2}N - s}\right)\frac{1}{\cancel{\left(\tfrac{1}{2} - \tfrac{s}{N}\right)}}^{N} = 0$$

$$\Rightarrow \quad \boxed{\frac{2mB}{\tau} = \log\left(\frac{N+2s}{N-2s}\right)}$$

Solving the spin excess in thermal equilibrium.

$$\frac{N+\langle 2S\rangle}{N-\langle 2S\rangle} = e^{2mB/\tau} \qquad \boxed{\langle 2S\rangle = N\,\frac{e^{2mB/\tau}-1}{e^{2mB/\tau}+1} = N\tanh\left(\frac{mB}{\tau}\right)}$$

Substitute $\langle S\rangle$ into Landau free energy to get the real F,

$$F(\tau) = F_L(\tau,\langle S\rangle) = N\tau\left[-\frac{\langle 2S\rangle}{N}\left(\frac{mB}{\tau}\right) + \frac{1}{2}\left(1+\frac{\langle 2S\rangle}{N}\right)\log\frac{1}{2}\left(1+\frac{\langle 2S\rangle}{N}\right)\right.$$

$\frac{\langle 2S\rangle}{N} = \tanh\left(\frac{mB}{\tau}\right) \rightarrow$

$$\left. + \frac{1}{2}\left(1-\frac{\langle 2S\rangle}{N}\right)\log\frac{1}{2}\left(1-\frac{\langle 2S\rangle}{N}\right)\right]$$

$$F(\tau) = N\tau\left[-\left(\frac{mB}{\tau}\right)\tanh\left(\frac{mB}{\tau}\right) - \log 2 + \frac{1}{2}\,\frac{\langle 2S\rangle}{N}\underbrace{\log\left(\frac{1+\langle 2S\rangle/N}{1-\langle 2S\rangle/N}\right)}_{2mB/\tau}\right.$$

$$\left. + \frac{1}{2}\log\left[\left(1+\frac{\langle 2S\rangle}{N}\right)\left(1-\frac{\langle 2S\rangle}{N}\right)\right]\right]$$

Making use the identity $1-\tanh^2 x = \operatorname{sech}^2 x = 1/\cosh^2 x$,

$$F(\tau) = N\tau\left[-\log 2 + \frac{1}{2}\log\operatorname{sech}^2\left(\frac{mB}{\tau}\right)\right]$$

$$= \underline{-N\tau\log\left[2\cosh\left(\frac{mB}{\tau}\right)\right]}$$

$\leftarrow$ Helmholtz free energy by minimizing $F_L(\tau,S)$

One can verify the above result by computing the partition function of a binary spin

$$\boxed{Z_1 = e^{mB/\tau} + e^{-mB/\tau} = 2\cosh\left(\frac{mB}{\tau}\right)} \rightarrow F_1 = -\tau\log Z_1$$

Because all spins are independent $F = F_1 + F_1 + \cdots + F_1 = NF_1$

$$F = NF_1 = -N\tau\log Z_1 = \underline{-N\tau\log\left[2\cosh\left(\frac{mB}{\tau}\right)\right]}$$

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