4.2. Statistical Mechanics

For a system with energies E_n, its partition function is defined as

$$Z_\beta = \sum_n e^{-\beta E_n} = \sum_n \left\langle E_n \,\middle|\, e^{-\beta H} \,\middle|\, E_n \right\rangle = \operatorname{Tr} e^{-\beta H} \tag{4.5}$$

where

$$\beta = \frac{1}{k_B T} = \text{inverse temperature}$$

$$k_B = 1.3806 \times 10^{-16}\ \text{erg}/K = \text{Boltzmann constant}$$

$$= 8.617 \times 10^{-5}\ \text{ev}/K$$

In natural units

$$[\beta] = \left[\frac{1}{\text{energy}}\right] = \left[\frac{\text{time}}{\hbar}\right] = \left[\frac{\text{length}}{\hbar c}\right] = L$$

In the canonical ensemble,

$$\frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{1}{Z_\beta} e^{-\beta E_n} = \text{probability of system in state of energy } E_n.$$

Given Z_β, all thermal averges of the system are known. For example

$$\langle E \rangle_\beta \equiv \frac{1}{Z_\beta} \sum_n E_n e^{-\beta E_n}$$

$$= \frac{1}{Z_\beta} \sum_n \left\langle E_n \,\middle|\, H e^{-\beta H} \,\middle|\, E_n \right\rangle = \frac{1}{Z_\beta} \operatorname{Tr}\left(H e^{-\beta H}\right)$$

$$= -\frac{1}{Z_\beta} \frac{\partial}{\partial \beta} Z_\beta$$

$$= -\frac{\partial}{\partial \beta} \ln Z_\beta \tag{4.6}$$

The Helmholtz free energy is given by

$$F_\beta = -\frac{1}{\beta} \ln Z_\beta \tag{4.7}$$

Note: In the lingos of thermodynamics,

$$F_\beta = U - T S \tag{4.7a}$$

where S is the entropy & the internal energy $U = \langle E \rangle_\beta$ is a function whose independent variables are all extensive, i.e.,

$$d U = T\, d S - P\, d V + \sum_i Y_i\, d X_i \tag{4.7b}$$

where X_i & Y_i are other extensive & intensive variables, respectively. Eq(4.7b) is known as the 1st law of thermodynamics.

Hence,

$$d F_\beta = -S\, d T - P\, d V + \sum_i Y_i X_i \tag{4.7c}$$

$$\rightarrow \quad S = -\frac{\partial F_\beta}{\partial T} = -\frac{d \beta}{d T} \frac{\partial F_\beta}{\partial \beta} = k_B \beta^2 \frac{\partial F_\beta}{\partial \beta}$$

$$P = -\frac{\partial F_\beta}{\partial V} \tag{4.8}$$

To show that the two definitions, eqs(4.7 & 4.7a), of F_β are compatible, we use eqs(4.6-7) to write

$$T\,S = U - F_\beta = -\frac{\partial}{\partial\beta}\ln Z_\beta + \frac{1}{\beta}\ln Z_\beta$$
$$= \beta\,\frac{\partial}{\partial\beta}\left(-\frac{1}{\beta}\ln Z_\beta\right) = \beta\,\frac{\partial F_\beta}{\partial\beta}$$

in agreement with eq(4.8).

Consider now the propagator (or transition amplitude)

$$Z_{a\,b} = \langle q_b, t_b \mid q_a, t_a \rangle$$
$$= \left\langle q_b, t_b \,\middle|\, e^{-i H (t_b - t_a)/\hbar} \,\middle|\, q_a, t_a \right\rangle \qquad (4.9)$$

Making the Wick rotation

$$t_b - t_a \to -i\,\beta\,\hbar$$

we have

$$Z_\beta = \mathrm{Tr}\, e^{-\beta H} = \int d\,q \left\langle q \,\middle|\, e^{-\beta H} \,\middle|\, q \right\rangle$$
$$= \int d\,q\, \langle q, -i\,\beta\,\hbar \mid q, 0 \rangle \qquad (4.11)$$

Switching to the imaginary time

$$\tau = i\,t \qquad (4.11a)$$

we have

$$d\,t = -i\,d\,\tau \qquad \frac{d\,q}{d\,t} = i\,\frac{d\,q}{d\,\tau} \equiv i\,\dot{q}$$

so that the propagator can be written as

$$\langle q_a, -i\,\beta\,\hbar \mid q_a, 0 \rangle = \int_{q_a}^{q_a} \mathcal{D}\,p\,\mathcal{D}\,q\, e^{-S/\hbar}$$

where

$$S = -i \int_0^{-i\beta\hbar} d\,t \left(p\,\frac{d\,q}{d\,t} - H\right)$$
$$= \int_0^{\beta\hbar} d\,\tau\,(H - i\,p\,\dot{q})$$

Hence, eq(4.10a) becomes

$$Z_\beta = \int d\,q_a \int_{q_a}^{q_a} \mathcal{D}\,p\,\mathcal{D}\,q\, \exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\,\tau\,(H - i\,p\,\dot{q})\right] \qquad (4.12)$$

For the special case

$$H = \frac{p^2}{2\,m} + V(q) \qquad (4.13)$$

the p integrals can be performed as in eq(2.50) of §2.2 so that

$$Z_\beta = \int d\,q_a \int_{q_a}^{q_a} \overline{\mathcal{D}}\,q\, \exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\,\tau\,\mathcal{L}(\dot{q}, q)\right] \qquad (4.14)$$

where

$$\mathcal{L}(\dot{q}, q) = \frac{1}{2}\,m\,\dot{q}^2 + V(q)$$

& $\overline{\mathcal{D}}\,q$ was defined in eq(2.62) of §2.3.

Note that only periodic paths of period $\beta\,\hbar$ are included in eq(4.14), in agreement with the Kubo-Martin-Schwinger (KNS) condition that all expectation values are periodic with period β. The KMS condition can be proved as follows. By definition, the thermal average of a Heiseinberg operator is

$$\langle O_H(t) \rangle_\beta = \frac{1}{Z_\beta} \operatorname{Tr}\left[O_H(t)\, e^{-\beta H}\right]$$
$$= \frac{1}{Z_\beta} \sum_n \left\langle E_n \,\middle|\, O_H(t)\, e^{-\beta E_n} \,\middle|\, E_n \right\rangle \qquad (4.15)$$

where, by eq(2.24),

$$O_H(t) = e^{i H t/\hbar}\, O_S\, e^{-i H t/\hbar}$$
$$\rightarrow \qquad O_H(t + i \beta \hbar) = e^{-\beta H}\, e^{i H t/\hbar}\, O_S\, e^{-i H t/\hbar}\, e^{\beta H}$$
$$= e^{-\beta H}\, O_H(t)\, e^{\beta H} \qquad (4.16)$$
$$\therefore \qquad \langle O_H(t + i \beta \hbar) \rangle_\beta = \frac{1}{Z_\beta} \sum_n \left\langle E_n \,\middle|\, e^{-\beta E_n}\, O_H(t) \,\middle|\, E_n \right\rangle$$
$$= \langle O_H(t) \rangle_\beta \qquad (4.17)$$

as claimed.

For imaginary times $\tau = i\,t$, we have

$$O_H(\tau) = e^{H \tau/\hbar}\, O_S\, e^{-H \tau/\hbar}$$
$$\langle O_H(\tau + \beta \hbar) \rangle_\beta = \langle O_H(\tau) \rangle_\beta \qquad (4.18)$$

This periodicity also exists in thermal averages of time-ordered products.

Combining eqs(4.7 & 4.12), we have

$$F_\beta = -\frac{1}{\beta} \ln\left\{ \int d q_a \int_{q_a}^{q_a} \mathcal{D} p\, \mathcal{D} q \exp\left[-\frac{1}{\hbar} \int_0^{\beta \hbar} d\tau \left(H - i\, p\, \dot{q} \right) \right] \right\} \qquad (4.19)$$

For a system of one free particle, eq(3.4) gives

$$\langle q, -i \beta \hbar \mid q, 0 \rangle = \left(\frac{m}{2 \pi \beta \hbar^2} \right)^{d/2}$$

where d is the dimension of the system. Hence

$$F_\beta = -\frac{1}{\beta} \ln\left\{ \int d q_a \left(\frac{m}{2 \pi \beta \hbar^2} \right)^{d/2} \right\}$$
$$= -\frac{1}{\beta} \ln\left\{ V \left(\frac{m}{2 \pi \beta \hbar^2} \right)^{d/2} \right\} \qquad (4.20)$$

where V is the volume of the system.

Using eq(8), we have

$$P = -\frac{\partial F_\beta}{\partial V} = \frac{1}{\beta V} = \frac{k_B T}{V} \qquad (4.20a)$$

which is the ideal gas law if we take V to be the effective volume occupied by each particle.

Let the ground state energy be E_g. Eq(4.5) can be written as

$$e^{\beta E_g} Z_\beta = \sum_n e^{-\beta (E_n - E_g)} = 1 + \sum_{n \neq g} e^{-\beta (E_n - E_g)}$$

By definition,

$$E_n > E_g \qquad \forall\ n \neq g$$
$$\rightarrow \qquad \lim_{\beta \to \infty} e^{\beta E_g} Z_\beta = 1 \qquad (4.21)$$

Taking the logarithm, we have

$$\lim_{\beta \to \infty} \left(\beta E_g + \ln Z_\beta \right) = 0$$

$$E_g = -\lim_{\beta\to\infty} \frac{1}{\beta} \ln Z_\beta \qquad (4.22)$$
$$= \lim_{\beta\to\infty} F_\beta = \lim_{T\to 0} F_\beta$$

For the 1-D oscillator considered in §3.3, combining eqs(3.54 & 3.60) give

$$\langle q, -i\beta\hbar \mid q, 0\rangle$$
$$= \sqrt{\frac{m\omega}{2\pi\hbar\sinh\beta\hbar\omega}} \exp\left\{-\frac{m\omega q^2}{\sinh\beta\hbar\omega}(\cosh\beta\hbar\omega - 1)\right\}$$

$$\to \qquad Z_\beta = \sqrt{\frac{m\omega}{2\pi\hbar\sinh\beta\hbar\omega}} \int_{-\infty}^{\infty} dq \exp\left\{-\frac{m\omega q^2}{\sinh\beta\hbar\omega}(\cosh\beta\hbar\omega - 1)\right\}$$
$$= \sqrt{\frac{m\omega}{2\pi\hbar\sinh\beta\hbar\omega}} \sqrt{\frac{\pi\sinh\beta\hbar\omega}{m\omega(\cosh\beta\hbar\omega - 1)}}$$
$$= \frac{1}{\sqrt{2(\cosh\beta\hbar\omega - 1)}}$$
$$= \frac{1}{2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)} \qquad (4.23)$$

Eq(4.22) then gives

$$E_g = \lim_{\beta\to\infty} \frac{1}{\beta} \ln\left(e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}\right)$$
$$= \frac{1}{2}\hbar\omega \qquad (4.24)$$

Adding a source term, eq(4.19) becomes a generating functional

$$F_\beta[J] = -\frac{1}{\beta} \ln\left\{\int dq_a \int_{q_a}^{q_a} \mathcal{D}p\,\mathcal{D}q \exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left(H - ip\dot{q} - Jq\right)\right]\right\} \quad (4.25)$$

All thermal average for time ordered products can be calculated from eq(4.25) by functional derivatives. For example,

$$\langle Q(\tau)\rangle_\beta = \frac{1}{Z_\beta} \mathrm{Tr}\left(Q(\tau)\, e^{-\beta H_J}\right)$$
$$= \frac{1}{Z_\beta}\int dq_a \int_{q_a}^{q_a} \mathcal{D}p\,\mathcal{D}q\, q(\tau) \exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left(H - ip\dot{q} - Jq\right)\right]$$
$$= -\beta\hbar \frac{\delta F_\beta[J]}{\delta J(\tau)} \equiv Q_\beta(\tau) \qquad (4.26)$$

Similarly to the derivation of eq(4.21), we have

$$\lim_{\beta\to\infty} Z_\beta = e^{-\beta E_g}$$

$$\to \qquad \lim_{\beta\to\infty} \langle T\{Q(\tau_1)\ldots\}\rangle_\beta = \lim_{\beta\to\infty} \frac{1}{Z_\beta} \sum_n e^{-\beta E_n} \langle E_n \mid T\{Q(\tau_1)\ldots\} \mid E_n\rangle$$
$$= \lim_{\beta\to\infty} \sum_n e^{-\beta(E_n - E_g)} \langle E_n \mid T\{Q(\tau_1)\ldots\} \mid E_n\rangle$$
$$= \left\langle E_g \mid T\{Q(\tau_1)\ldots\} \mid E_g\right\rangle \qquad (4.27)$$

In other words, the path integral that includes only periodic paths of infinite periodicity serves as a generator for ordered products between ground states.

For example, for the harmonic oscillator,

$$\lim_{\beta \to \infty} \langle Q_H(0)^2 \rangle_\beta = \langle 0 \mid Q^2 \mid 0 \rangle$$

$$= \frac{\hbar}{2 m \omega} \langle 0 \mid (a + a^+)^2 \mid 0 \rangle$$

$$= \frac{\hbar}{2 m \omega} \tag{4.28}$$

The generating functional $\Gamma_\beta[Q_\beta]$, also known as the effective action, is related to $F_\beta[J]$ by a Legendre transform

$$\Gamma_\beta[Q_\beta] = F_\beta[J] + \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\tau \, J(\tau) \, Q_\beta(\tau) \tag{4.29}$$

Using the chain rule, we have

$$\frac{\delta F_\beta[J]}{\delta Q_\beta(\tau)} = \int_0^{\beta \hbar} d\tau' \frac{\delta J(\tau')}{\delta Q_\beta(\tau)} \frac{\delta F_\beta[J]}{\delta J(\tau')}$$

$$\rightarrow \qquad \frac{\delta \Gamma_\beta[Q_\beta]}{\delta Q_\beta(\tau)} = \int_0^{\beta \hbar} d\tau' \frac{\delta F_\beta[J]}{\delta J(\tau')} \frac{\delta J(\tau')}{\delta Q_\beta(\tau)} + \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\tau' \frac{\delta J(\tau')}{\delta Q_\beta(\tau)} Q_\beta(\tau) \tag{4.30}$$

$$+ \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\tau' \, J(\tau') \frac{\delta Q_\beta(\tau')}{\delta Q_\beta(\tau)}$$

By eq(4.26), the first 2 terms cancel, so that

$$\frac{\delta \Gamma_\beta[Q_\beta]}{\delta Q_\beta(\tau)} = \frac{1}{\beta \hbar} J(\tau) \tag{4.31}$$

In the equilibrium state $J = 0$. Eq(4.31) then implies the equilibrium condition

$$\frac{\delta \Gamma_\beta[Q_\beta]}{\delta Q_\beta(\tau)} = 0 \tag{4.32}$$

Taking another functional derivative on eq(4.31) gives

$$\beta \frac{\delta^2 \Gamma_\beta[Q_\beta]}{\delta Q_\beta(\tau) \, \delta Q_\beta(\tau')} = \frac{1}{\hbar} \frac{\delta J(\tau')}{\delta Q_\beta(\tau)} \equiv P_\beta(\tau', \tau) \tag{4.33}$$

Similarly, eq(4.26) gives

$$\hbar \frac{\delta Q_\beta(\tau)}{\delta J(\tau')} = -\beta \hbar^2 \frac{\delta^2 F_\beta[J]}{\delta J(\tau') \, \delta J(\tau)}$$

$$= \langle T \{ Q(\tau) \, Q(\tau') \} \rangle_\beta \equiv G_\beta(\tau, \tau') \tag{4.34}$$

where the imaginary time-ordering works the same as the real time version

$$T \{ A(\tau) \, B(\tau') \} = \theta(\tau - \tau') \, A(\tau) \, B(\tau') + \theta(\tau' - \tau) \, B(\tau') \, A(\tau) \tag{4.35}$$

$$\int_0^{\beta \hbar} d\tau_1 \, P_\beta(\tau, \tau_1) \, G_\beta(\tau_1, \tau') = \int_0^{\beta \hbar} d\tau_1 \frac{\delta J(\tau)}{\delta Q_\beta(\tau_1)} \frac{\delta Q_\beta(\tau_1)}{\delta J(\tau')}$$

$$= \frac{\delta J(\tau)}{\delta J(\tau')} = \delta(\tau - \tau') \tag{4.36}$$

Thus, P_β & G_β are functional inverse to each other. Further discussions on Γ_β can be found in Chap 8.