2.9. Density Matrix

Local information is contained in the density operator

$$\hat{\rho} \equiv \frac{1}{Z} e^{-\hat{H}/k_B T} = \frac{1}{Z} e^{-\beta \hat{H}} \tag{2.340a}$$

For example, its diagonal elements in the x-representation

$$\rho(\boldsymbol{x}) = \frac{1}{Z} \left\langle \boldsymbol{x} \,\middle|\, e^{-\beta \hat{H}} \,\middle|\, \boldsymbol{x} \right\rangle \tag{2.340}$$

gives the probability of a particle to be at $\boldsymbol{x}$ when the system is at temperature T. Using the definition (2.332) of Z, we obtained the requisite sum rule for probabilities

$$\int d\boldsymbol{x}\, \rho(\boldsymbol{x}) = 1 \tag{2.341}$$

Let $\psi_n(\boldsymbol{x}) = \langle \boldsymbol{x} \mid n \rangle$ be a complete set of orthonormal eigenfunctions of $\hat{H}$ with eigenvalues E_n. The spectral decomposition of $\rho(\boldsymbol{x})$ gives

$$\begin{aligned} \rho(\boldsymbol{x}) &= \frac{1}{Z} \sum_{n,m} \langle \boldsymbol{x} \mid m \rangle \left\langle m \,\middle|\, e^{-\beta \hat{H}} \,\middle|\, n \right\rangle \langle n \mid \boldsymbol{x} \rangle \\ &= \frac{1}{Z} \sum_{n,m} \langle \boldsymbol{x} \mid m \rangle\, \delta_{mn}\, e^{-\beta E_n} \langle n \mid \boldsymbol{x} \rangle \\ &= \frac{1}{Z} \sum_{n} e^{-\beta E_n}\, \psi_n(\boldsymbol{x})\, \psi_n^*(\boldsymbol{x}) \\ &= \frac{1}{\sum_n e^{-\beta E_n}} \sum_n e^{-\beta E_n} \left| \psi_n(\boldsymbol{x}) \right|^2 \end{aligned} \tag{2.342}$$

Since $|\psi_n(\boldsymbol{x})|^2$ is the probability density of the state $|\, n \rangle$, and $\frac{1}{Z} e^{-\beta E_n}$ is the probability of the system at temperature T being in state $|\, n \rangle$, we see that $\frac{1}{Z} e^{-\beta E_n} |\psi_n(\boldsymbol{x})|^2$ gives the probability of finding a particle at $\boldsymbol{x}$ if the system is in state $|\, n \rangle$. Summing over all n then gives the probability of a particle to be at $\boldsymbol{x}$, irregardless of the state of the system. Thus our stated interpretation of $\rho(\boldsymbol{x})$.

As $T \to 0$, $\beta \to \infty$. The leading term in the sum over n is therefore the ground state:

$$\rho(\boldsymbol{x}) \xrightarrow[T \to 0]{} \frac{e^{-\beta E_0}}{e^{-\beta E_0}} |\psi_0(\boldsymbol{x})|^2 = |\psi_0(\boldsymbol{x})|^2 \tag{2.343}$$

As $T \to \infty$, $\beta \to 0$. Quantum effects are expected to become irrelevant. Since

$$Z \xrightarrow[T \to \infty]{} Z_{\text{cl}} = \int d\boldsymbol{x} \int \frac{d\boldsymbol{p}}{(2\pi\hbar)^D} e^{-\beta H(\boldsymbol{x},\boldsymbol{p})} \tag{2.344}$$

we expect

$$\rho(\boldsymbol{x}) \xrightarrow[T \to \infty]{} \rho_{\text{cl}}(\boldsymbol{x}) = \frac{1}{Z_{\text{cl}}} \int \frac{d\boldsymbol{p}}{(2\pi\hbar)^D} e^{-\beta H(\boldsymbol{x},\boldsymbol{p})} \tag{2.345}$$

Comment:

1. In classical statistical mechanics, Z_{cl} is defined only up to an overall constant. The factor $(2\pi\hbar)^{-D}$ was chosen to agree with the quantum version.
2. D is the degrees of freedom of the system. For a system of N particles in 3-D, $D = 3N$.

A better justification of (2.344-5) is as follows. For T large, $\tau_b - \tau_a = \hbar\beta$ is small so that one time slice ($N = 0$, $\epsilon = \hbar\beta$) is sufficient and (2.332a) reduces to

$$Z \approx \int d\boldsymbol{x} \left\langle \boldsymbol{x} \left| e^{-\epsilon \hat{H}/\hbar} \right| \boldsymbol{x} \right\rangle \tag{2.346}$$

while (2.333) becomes

$$\left\langle \boldsymbol{x} \left| e^{-\epsilon \hat{H}/\hbar} \right| \boldsymbol{x} \right\rangle = \int \frac{d\boldsymbol{p}}{(2\pi\hbar)^D} \exp\left[-\frac{\epsilon}{\hbar} H(\boldsymbol{x}, \boldsymbol{p}) \right] \tag{2.347}$$

so that (2.346) is just (2.344). (2.345) then follows.

Physically speaking, as the (imaginary) time interval $\beta \to 0$, there is no time for the system path to fluctuate from its classical path. Hence, only one term is required in the product of (2.332). More detailed discussion can be found in §2.13.

Consider now the standard Hamiltonian

$$H(\boldsymbol{x}, \boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2M} + V(\boldsymbol{x}) \tag{2.348}$$

Using

$$\int_{-\infty}^{\infty} dx\, e^{-a x^2/2} = \sqrt{\frac{2\pi}{a}} \tag{2.349a}$$

we have, with $a = \frac{\epsilon}{M\hbar} \approx \frac{\beta}{M}$,

$$\int \frac{d\boldsymbol{p}}{(2\pi\hbar)^D} \exp\left[-\frac{\epsilon}{\hbar} H(\boldsymbol{x}, \boldsymbol{p}) \right] \approx \left(\frac{M}{2\pi\hbar^2\beta} \right)^{D/2} \exp\left[-\beta V(\boldsymbol{x}) \right]$$

so that (2.344) becomes

$$\begin{aligned} Z_{\text{cl}} &= \left(\frac{M}{2\pi\hbar^2\beta} \right)^{D/2} \int d\boldsymbol{x} \exp\left[-\beta V(\boldsymbol{x}) \right] \\ &= \int \frac{d\boldsymbol{x}}{l_e^D} e^{-\beta V(\boldsymbol{x})} \end{aligned} \tag{2.350}$$

where the thermal length is defined as

$$l_e = \sqrt{\frac{2\pi\hbar^2\beta}{M}} = \sqrt{\frac{2\pi\hbar^2}{M k_B T}} \tag{2.351}$$

is the Euclidean analog of the characteristic length defined in (2.126) for real-times. It is also known as the de Broglie wavelength associated with the temperature $T = \frac{1}{k_B \beta}$, or, in short, the thermal de Broglie wavelength.

(2.345) then becomes

$$\rho(\boldsymbol{x}) \xrightarrow[T\to\infty]{} \rho_{\text{cl}}(\boldsymbol{x}) = \frac{1}{Z_{\text{cl}}\, l_e^D} e^{-\beta V(\boldsymbol{x})} \tag{2.352}$$

For a free particle confined in a box of side-length L, (2.350) becomes

$$Z_{\text{cl}} = \left(\frac{L}{l_e} \right)^D \tag{2.354}$$

For a 1-D harmonic oscillator,

$$Z_{\text{cl}} = \int_{-\infty}^{\infty} \frac{dx}{l_e} e^{-\beta M \omega^2 x^2/2}$$

Using (2.349a) with $a = \beta M \omega^2$, we have

$$Z_{\text{cl}} = \frac{1}{l_e} \sqrt{\frac{2\pi}{\beta M \omega^2}} = \frac{l_\omega}{l_e} \tag{2.355a}$$

where

$$l_\omega = \sqrt{\frac{2\pi}{\beta M \omega^2}} \qquad (2.356)$$

is the classical length scale of the oscillator.

Generalization to D-D is trivial:

$$Z_{\rm cl} = \left(\frac{l_\omega}{l_e}\right)^D \qquad (2.355)$$

Combining (2.351) & (2.356) gives

$$l_\omega l_e = \sqrt{\frac{2\pi}{\beta M \omega^2}} \sqrt{\frac{2\pi\hbar^2\beta}{M}} = \frac{2\pi\hbar}{M\omega} = 2\pi\lambda_\omega^2$$

where λ_ω is the quantum length scale of the oscillator defined in (2.350).

Comparing (2.354) with (2.355) gives us a mnemonic rule:

$$l_\omega \xrightarrow[\omega\to 0]{} L \qquad (2.358)$$

which transforms the properties of an oscillator to those of a free particle.

Using (2.356), this rule becomes

$$\frac{1}{\omega} \xrightarrow[\omega\to 0]{} \sqrt{\frac{\beta M}{2\pi}}\, L \qquad (2.359)$$

The real time version is therefore

$$\frac{1}{\omega} \xrightarrow[\omega\to 0]{} \sqrt{\frac{i(t_b - t_a)\, M}{2\pi\hbar}}\, L \qquad (2.360)$$

The path integral representation of $\rho(\boldsymbol{x})\, Z$ can be obtained from that for Z by removing the trace operation but keeping the periodic B.C. Thus, (2.337) gives

$$\rho(\boldsymbol{x}_a) = \frac{1}{Z}\int_{\boldsymbol{x}(0)=\boldsymbol{x}_a}^{\boldsymbol{x}(\hbar\beta)=\boldsymbol{x}_a} \mathcal{D}'\boldsymbol{x} \int \frac{\mathcal{D}\boldsymbol{p}}{(2\pi\hbar)^D}\, e^{-\mathcal{A}_e[\boldsymbol{x},\boldsymbol{p}]/\hbar} \qquad (2.361a)$$

$$= \frac{1}{Z}\int_{\boldsymbol{x}(0)=\boldsymbol{x}_a}^{\boldsymbol{x}(\hbar\beta)=\boldsymbol{x}_a} \mathcal{D}\boldsymbol{x}\; e^{-\mathcal{A}_e[\boldsymbol{x}]/\hbar} \qquad (2.361)$$

where $\mathcal{A}_e[\boldsymbol{x}, \boldsymbol{p}]$ is given by (2.336),

$$\mathcal{A}_e[\boldsymbol{x}, \boldsymbol{p}] = \int_0^{\beta\hbar} d\tau\, (-i\,\boldsymbol{p}\cdot\boldsymbol{x}' + H) \qquad \boldsymbol{x}' = \frac{d\boldsymbol{x}}{d\tau}$$

and [see (2.338)]

$$\mathcal{A}_e[\boldsymbol{x}] = \int_0^{\beta\hbar} d\tau\, L_e \qquad (2.361b)$$

Thermal equilibrium expectation of an arbitrary Hermitian operator $\hat{O}$ is given by

$$\langle \hat{O} \rangle_T \equiv \mathrm{Tr}\left(\hat{\rho}\,\hat{O}\right) = \mathrm{Tr}\left(\hat{O}\,\hat{\rho}\right)$$

$$= \frac{1}{Z}\mathrm{Tr}\left(e^{-\beta\hat{H}}\,\hat{O}\right) = \frac{1}{Z}\mathrm{Tr}\left(\hat{O}\, e^{-\beta\hat{H}}\right) \qquad (2.362a)$$

With respect to the energy eigenstates,

$$\langle \hat{O} \rangle_T = \frac{1}{Z}\sum_n \left\langle n \,\middle|\, e^{-\beta\hat{H}}\,\hat{O} \,\middle|\, n \right\rangle$$

$$= \frac{1}{Z} \sum_n e^{-\beta E_n} \left\langle n \mid \hat{O} \mid n \right\rangle \tag{2.362}$$

In terms of the local basis,

$$\langle \hat{O} \rangle_T = \frac{1}{Z} \iint d\,\boldsymbol{x}_b\, d\,\boldsymbol{x}_a \left\langle \boldsymbol{x}_b \,\middle|\, e^{-\beta \hat{H}} \,\middle|\, \boldsymbol{x}_a \right\rangle \left\langle \boldsymbol{x}_a \mid \hat{O} \mid \boldsymbol{x}_b \right\rangle \tag{2.363}$$

$$\rightarrow \qquad \left\langle f(\hat{\boldsymbol{x}}) \right\rangle_T = \frac{1}{Z} \iint d\,\boldsymbol{x}_b\; d\,\boldsymbol{x}_a \left\langle \boldsymbol{x}_b \,\middle|\, e^{-\beta \hat{H}} \,\middle|\, \boldsymbol{x}_a \right\rangle \delta(\boldsymbol{x}_a - \boldsymbol{x}_b)\, f(\boldsymbol{x}_b)$$

$$= \frac{1}{Z} \int d\,\boldsymbol{x}_b \left\langle \boldsymbol{x}_b \,\middle|\, e^{-\beta \hat{H}} \,\middle|\, \boldsymbol{x}_b \right\rangle f(\boldsymbol{x}_b)$$

$$= \int d\,\boldsymbol{x}\, \rho(\boldsymbol{x})\; f(\boldsymbol{x}) \qquad \text{[(2.340) used.]} \tag{2.364}$$

in agreement of the probability interpretation of $\rho(\boldsymbol{x})$ stated after (2.340).

If f also depends on $\boldsymbol{p}$, then (2.363) requires also the off diagonal elements of the density matrix

$$\rho(\boldsymbol{x}_b, \boldsymbol{x}_a) = \frac{1}{Z} \left\langle \boldsymbol{x}_b \,\middle|\, e^{-\beta \hat{H}} \,\middle|\, \boldsymbol{x}_a \right\rangle \tag{2.365}$$

In contrast to the “pure state” density matrix introduced for one quantum state in (1.221), (2.365) defines a “mixed state” density matrix.

Using (2.365), (2.340) becomes

$$\rho(\boldsymbol{x}) = \rho(\boldsymbol{x}, \boldsymbol{x}) \tag{2.365a}$$

To keep the analogy between quantum mechanics and quantum statistics as close as possible, we introduce the evolution operator along the imaginary time axis as

$$\hat{U}_e(\tau_b, \tau_a) \equiv e^{-(\tau_b - \tau_a)\hat{H}/\hbar} \qquad \tau_b > \tau_a \tag{2.366}$$

together with the Euclidean (or imaginary) time evolution amplitude

$$(\boldsymbol{x}_b\, \tau_b \mid \boldsymbol{x}_a\, \tau_a) \equiv \left\langle \boldsymbol{x}_b \,\middle|\, \hat{U}_e(\tau_b, \tau_a) \,\middle|\, \boldsymbol{x}_a \right\rangle \qquad \tau_b > \tau_a \tag{2.367}$$

The condition $\tau_b > \tau_a$ was introduced so that system with no upper bound to its energy spectrum can be treated.

(2.332) can now be written as

$$Z = \int d\,\boldsymbol{x}\, (\boldsymbol{x}, \beta\hbar \mid \boldsymbol{x}\, 0) \tag{2.368}$$

and (2.365) as

$$\rho(\boldsymbol{x}_b, \boldsymbol{x}_a) = \frac{1}{Z} (\boldsymbol{x}_b, \beta\hbar \mid \boldsymbol{x}_a\, 0) \tag{2.269}$$

For a time-dependent Hamiltonian, (2.366) must be replaced by

$$\hat{U}_e(\tau_b, \tau_a) = \hat{T}_\tau \exp\left[-\frac{1}{\hbar} \int_{\tau_a}^{\tau_b} d\,\tau\, \hat{H}(-i\,\tau)\right] \tag{2.270}$$

which is obtained from (1.252) by the transform $t \rightarrow -i\,\tau$. $\hat{T}_\tau$ is an order operator that puts operators with larger τ to the left.

It must be emphasized that a time-dependent H can be reconciled with the equilibrium assumption of the ensemble theory of statistical mechanics only when the time-scale of change in H is much larger than the relaxation time required to re-establish equilibrium. The theory of linear response is based on this assumption and is discussed in Chapter 18.

The study of a general time-dependent H falls into the purvey of non-equilibrium statistical mechanics.

One should by now be familiar enough with the formulism to write down the time-sliced path integral representation for (2.367) immediately

$$(\boldsymbol{x}_b\,\tau_b \mid \boldsymbol{x}_a\,\tau_a) = \left(\prod_{k=1}^{N}\int d\,\boldsymbol{x}_k\right)\left(\prod_{n=1}^{N+1}\int\frac{d\,\boldsymbol{p}_n}{(2\,\pi\,\hbar)^D}\right)\exp\left(-\frac{1}{\hbar}\mathcal{A}_e^N\right) \qquad (2.371)$$

where

$$\mathcal{A}_e^N = \sum_{n=1}^{N+1}\left[\,-i\,\boldsymbol{p}_n\cdot(\boldsymbol{x}_n-\boldsymbol{x}_{n-1})+\epsilon\,H(\boldsymbol{x}_n,\,\boldsymbol{p}_n,\,\tau_n)\right] \qquad (2.372)$$

and

$$H(\boldsymbol{x}_n,\,\boldsymbol{p}_n,\,\tau_n) = H(\boldsymbol{x}_n,\,\boldsymbol{p}_n,\,t)\Big|_{t=-i\,\tau_n}$$

In the continuum limit,

$$(\boldsymbol{x}_b\,\tau_b \mid \boldsymbol{x}_a\,\tau_a) = \int\mathcal{D}'\,\boldsymbol{x}\int\frac{\mathcal{D}\,\boldsymbol{p}}{(2\,\pi\,\hbar)^D}\exp\left(-\frac{1}{\hbar}\mathcal{A}_e[\boldsymbol{x},\,\boldsymbol{p}]\right) \qquad (2.273)$$

Consider a standard Hamiltonian of the form (2.7),

$$H(\boldsymbol{x},\,\boldsymbol{p},\,\tau) = \frac{1}{2\,M}\boldsymbol{p}^2 + V(\boldsymbol{x},\,\tau)$$

If V is smooth, the momenta can be integrated out as in (2.51-3). Hence,

$$(\boldsymbol{x}_b\,\tau_b \mid \boldsymbol{x}_a\,\tau_a) = \left(\frac{M}{2\,\pi\,\hbar\,\epsilon}\right)^{(N+1)\,D/2}\left(\prod_{k=1}^{N}\int d\,\boldsymbol{x}_k\right) \qquad (2.274)$$

$$\times\exp\left\{-\frac{1}{\hbar}\,\epsilon\sum_{n=1}^{N+1}\left[\frac{1}{2}M\left(\frac{\boldsymbol{x}_n-\boldsymbol{x}_{n-1}}{\epsilon}\right)^2+V(\boldsymbol{x}_n,\,\tau_n)\right]\right\}$$

$$= \int\mathcal{D}\,\boldsymbol{x}\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\,\tau\,L_e\right) \qquad (2.274a)$$

where

$$L_e = \frac{1}{2}M\,\boldsymbol{x}'^{\,2}+V(\boldsymbol{x},\,\tau) \qquad \boldsymbol{x}' = \frac{d\,\boldsymbol{x}}{d\,\tau} \qquad (2.274b)$$

(2.368) then becomes

$$Z = \oint\mathcal{D}\,\boldsymbol{x}\exp\left(-\frac{1}{\hbar}\mathcal{A}_e[\boldsymbol{x}]\right) \qquad (2.375)$$

where

$$\mathcal{A}_e[\boldsymbol{x}] = \int_0^{\beta\hbar}d\,\tau\,L_e = \int_0^{\beta\hbar}d\,\tau\left[\frac{1}{2}M\,\boldsymbol{x}'^{\,2}+V(\boldsymbol{x},\,\tau)\right] \qquad (2.376)$$

$$\oint\mathcal{D}\,\boldsymbol{x} = \left(\frac{M}{2\,\pi\,\hbar\,\epsilon}\right)^{(N+1)\,D/2}\left(\prod_{k=1}^{N+1}\int_{\text{All space}}d\,\boldsymbol{x}_k\right)_{\boldsymbol{x}_{N+1}=\boldsymbol{x}_0} \qquad (2.377)$$

The periodic B.C., $\boldsymbol{x}(\beta\,\hbar)=\boldsymbol{x}(0)$, can be enforced by expanding $\boldsymbol{x}(\tau)$ into a Fourier series

$$x(\tau) = \sum_{m=-\infty}^{\infty}e^{-i\,\omega_m\,\tau}\,x_m \qquad (2.378)$$

where

$$\omega_m = \frac{2\,\pi\,k_B\,T}{\hbar}\,m = \frac{2\,\pi}{\beta\,\hbar}\,m, \qquad m=0,\,\pm1,\,\pm2,\,\ldots \qquad (2.379)$$

are called Matsubara frequencies. Using (2.378), we can extend $\boldsymbol{x}$ over the entire imaginary axis as a periodic function

$$\boldsymbol{x}(\tau+\beta\,\hbar) = \boldsymbol{x}(\tau) \qquad (2.380)$$

The path integral (2.377) thus consists of integrations over periodic paths of period $\beta\hbar$. In the time-sliced version (2.274), only $\boldsymbol{x}(\tau)$ at discrete times $\tau_n = n\,\epsilon = n\,\frac{\beta\hbar}{N+1}$ are needed. Since only there are only $N+1$ non-equivalent x_n points, (2.378) reduces to a finite sum of $N+1$ terms:

$$x_n \equiv x(\tau_n) = \frac{1}{\sqrt{N+1}} \sum_m e^{-i\,\omega_m \tau_n}\, x_m \tag{2.380a}$$

with the range of m determined by the condition

$$\omega_m \tau_n = \frac{2\pi}{\beta\hbar}\, m\, n\, \epsilon = \frac{2\pi}{N+1}\, m\, n \in [-\pi, \pi]$$

At the endpoints, we have

$$\frac{2\pi}{N+1}\, m_e = \mp\pi \rightarrow \qquad m_e = \mp \text{Floor}\left(\frac{N+1}{2}\right)$$

For N even, we have $m_e = \mp\frac{N}{2}$ so that $m = -\frac{N}{2},\ \ldots,\ 0,\ \ldots,\ \frac{N}{2}$.

For N odd, we have $m_e = \mp\frac{N+1}{2}$. Since only $N+1$ points are needed, we have either $m = -\frac{N-1}{2},\ \ldots,\ 0,\ \ldots,\ \frac{N+1}{2}$ or $m = -\frac{N+1}{2},\ \ldots,\ 0,\ \ldots,\ \frac{N-1}{2}$.

Taking the complex conjugate of (2.380a) gives

$$x_n^* = x(\tau_n)^* = \frac{1}{\sqrt{N+1}} \sum_m e^{i\,\omega_m \tau_n}\, x_m^*$$

From (2.379), we have

$$\omega_{-m} = -\omega_m$$

For N even, we have

$$x_n^* = x(\tau_n)^* = \frac{1}{\sqrt{N+1}} \sum_{m=-N/2}^{N/2} e^{i\,\omega_m \tau_n}\, x_m^* = \frac{1}{\sqrt{N+1}} \sum_{m=-N/2}^{N/2} e^{-i\,\omega_m \tau_n}\, x_{-m}^*$$

so that $x(\tau_n)$ is real implies

$$x_{-m}^* = x_m \qquad \text{for}\ \ m = -\frac{N}{2},\ \ldots,\ 0,\ \ldots,\ \frac{N}{2} \tag{2.381a}$$

For N odd, we have

$$x_n^* = x(\tau_n)^* = \frac{1}{\sqrt{N+1}} \sum_{m=-(N-1)/2}^{(N+1)/2} e^{i\,\omega_m \tau_n}\, x_m^* = \frac{1}{\sqrt{N+1}} \sum_{m=-(N+1)/2}^{(N-1)/2} e^{-i\,\omega_m \tau_n}\, x_{-m}^*$$

so that $x(\tau_n)$ is real implies

$$x_{-m}^* = x_m \tag{2.381b}$$

for $m = -\frac{N-1}{2},\ \ldots,\ 0,\ \ldots,\ \frac{N-1}{2}$ plus either $m = -\frac{1}{2}(N+1)$ or $m = \frac{1}{2}(N+1)$.

See Kleinert's comparison between ω_m & ν_m in the last paragraph of text.