

CHAPTER II

QUANTUM STATISTICAL MECHANICS

AND DENSITY MATRIX

2.1 CANONICAL DISTRIBUTION, PARTITION FUNCTION AND FREE ENERGY [1]

The old method used in finding some important quantities of the system at a give temperature was based on the macroscopic aspects of the general theory of statistical thermodynamics. However it was discovered that greater insight and power could be gained by considering also the microscopic aspects of the theory. Therefore, some important ideas for microscopic theory will be reviewed as follows: Normally the system is classified in to two categories. First, the "isolated system" and second, the "system in contact with a reservoir." The isolated system is the system which maintains its energy and number of particles all the time i.e., It doesn't exchange its energy and number of particles with another system. In the real nature, such a system may not occur because when we look at a particular system, we frequently find something interacting with the system in some ways. By these reasons, it is more advantageous to study the system in contact with a reservoir than the isolated system. The reservoir can not be isolately defined, it must be defined with respect to the system in contact with it. It is defined as the system which has larger degree of freedom than that of the system in contact with it. The question then arises, how much degree of freedom than that of the system in contact with it. The question arises, how much degree of freedom does the reservoir need? The answer is that it needs more degrees of freedom than what the system needs to make the reservoir's temperature(chemical potential) remain unaffected by whatever small amount of energy (particles) it gives to the system.

Now, let's consider the system in contact with a (heat) reservoir which exchanges only the energy by each other. In thermal equilibrium situation the interaction between the system and the reservoir is weak so that their energy are additive, then the probability of the system is in state r is $P_r \propto e^{-\beta E_r}$ where $\beta = (k_B T)^{-1}$, k_B is Boltzmann constant and T is the temperature of the system which equals to the temperature of the reservoir. Since the probability must be normalized, the form of the probability is

$$P_r = \frac{e^{-\beta E_r}}{Z} \quad (2.1)$$

where

$$Z = \sum_r e^{-\beta E_r} \quad (2.2)$$

Here \sum_r is the summation over all accessible states of the system.

The exponential factor $e^{-\beta E_r}$ is called the "Boltzmann factor"; the corresponding probability distribution eq. (2.1) and the ensemble is known as the "canonical distribution" and "canonical ensemble" respectively. Z in eq. (2.2) is called the "partition function." By using this partition function, the (Helmholtz) free energy F is defined by the following relation

$$e^{-\beta F} = Z \quad (2.3)$$

To understand the physical meaning of free energy, let's substitute eq. (2.3) into eq. (2.1) which shows that the normalized probability is $P_r = e^{-\beta(E_r - F)}$. By this equation, it is clear that the free energy represents most of the energy of the systems in the canonical ensemble. Note that if there exists state r such that $E_r = F$, then the system is in "pure state" r i.e., the system is in state r only (with probability $P_r = 1$).

Eq. (2.1) and eq. (2.2) are not restricted to be used only in classical or quantum mechanics since the accessible states are general. They can be both discrete and continuous.

2.2 DENSITY OPERATOR AND DENSITY MATRIX [2]

In quantum mechanical problem, we usually act as if the system we are interested in comprised the entire universe. Now, let us see what happens if we divide the entire universe into a system and the rest of the universe.

Let $|\varphi_i\rangle$ be a complete set of vectors in vector space describing the system, and let $|\theta_j\rangle$ be a complete set for the rest of the universe. The most general vector (state) in the entire vector space can be written as

$$|\psi\rangle = \sum_{i,j} c_{ij} |\varphi_i\rangle |\theta_j\rangle \quad (2.4)$$

Let \hat{A} be the operator on the entire vector space that acts only on the system. When \hat{A} acts on product state (e.g., $|\varphi_i\rangle|\theta_j\rangle$) we really mean $\hat{A}|\varphi_i\rangle|\theta_j\rangle = (\hat{A}|\varphi_i\rangle)|\theta_j\rangle$. So, we can write \hat{A} in the form of

$$\hat{A} = \sum_{i,i'} A_{ii'} |\varphi_i\rangle|\theta_j\rangle\langle\theta_j|\langle\varphi_{i'}| \quad (2.5)$$

where $A_{ii'} = \langle\varphi_i|\hat{A}|\varphi_{i'}\rangle$ is the matrix element of \hat{A} in the basis of vector space describing the system.

From eq. (2.4) and eq. (2.5), we can find the expectation value of \hat{A} with respect to general state $|\psi\rangle$,

$$\begin{aligned} \langle\hat{A}\rangle &= \langle\psi|\hat{A}|\psi\rangle = \sum_{i,i',j,j'} c_{ij}^* c_{i'j} \langle\theta_j|\langle\varphi_i|\hat{A}|\varphi_{i'}\rangle|\theta_j\rangle \\ &= \langle\varphi_i|\hat{A}|\varphi_{i'}\rangle \rho_{i'i} \end{aligned} \quad (2.6)$$

where

$$\rho_{i'i} = \sum_j c_{ij}^* c_{i'j} \quad (2.7)$$

$\rho_{i'i}$ in eq. (2.7) is called the "density matrix". From this equation, we can define the "density operator" $\hat{\rho}$ by

$$\rho_{i'i} = \langle\varphi_i|\hat{\rho}|\varphi_{i'}\rangle \quad (2.8)$$

where $\hat{\rho}$ operates only on the system.

Inserting eq. (2.8) into eq. (2.6), we get

$$\begin{aligned} \langle\hat{A}\rangle &= \sum_i \langle\varphi_i|\hat{A}\left(\sum_{i'} |\varphi_{i'}\rangle\langle\varphi_{i'}|\right)\hat{\rho}|\varphi_i\rangle \\ &= \sum_i \langle\varphi_i|\hat{A}\hat{\rho}|\varphi_i\rangle = \text{Tr}(\hat{A}\hat{\rho}) = \text{Tr}(\hat{\rho}\hat{A}) \end{aligned} \quad (2.9)$$

where the symbol "Tr" is called the "trace" which represents the diagonal sum of the matrix elements. From eq. (2.7) and eq. (2.8), it is obvious that $\hat{\rho}$ is hermitian. Therefore, it can be diagonalized with a complete orthonormal set of eigen vectors $|i\rangle$ and real eigen value w_i ,

$$\hat{\rho} = \sum_i w_i |i\rangle\langle i| \quad (2.10)$$

From eq. (2.9) and eq. (2.10), one can reformulate quantum mechanics as follows [2]:

Any system is described by a density operator $\hat{\rho}$, where $\hat{\rho}$ is of the form $\sum_i w_i |i\rangle\langle i|$ and

- a) the set $|i\rangle$ is a complete orthonormal set of vectors.
- b) $w_i \geq 0$
- c) $\sum_i w_i = 1$
- d) Given an operator \hat{A} , the expectation of \hat{A} is given by

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho}\hat{A})$$

Notice that

$$\begin{aligned} \langle \hat{A} \rangle &= \text{Tr}(\hat{\rho}\hat{A}) = \sum_i \langle i' | \hat{\rho}\hat{A} | i' \rangle \\ &= \sum_i w_i \langle i | \hat{A} | i \rangle \end{aligned} \quad (2.11)$$

From eq. (2.11) and properties b) and c) above, one can interpret w_i as the probability that the system is in state $|i\rangle$. Since w_i is an eigen value of $\hat{\rho}$, one can conclude that the density matrix is the quantity that contains all about the information of the rest of the universe which influences the system. We can look at this fact directly by considering eq. (2.7). Since $\rho_{i,i}$ ($= w_i \delta_{i,i}$ for basis $|i\rangle$) comes from the sum over state index j which is the index describes the state in the rest of the universe, $\rho_{i,i}$ will effectively contain the behaviors of the rest of the universe that influence the system. Now, the question arises, how does the rest of the universe influence the system? The answer is that when we fix the system state index i there are many types of vector which correspond to index i in the rest of the universe. These many types of vector are not the same for each system index i . By this reason, many different types of vector in the rest of the universe corresponding to different index i constitute the different probability w_i for each i . To understand this concept more clearly, let's consider the following equations:

Let x describe the coordinate of the system. From eq. (2.9), we have

$$\begin{aligned} \langle \hat{A} \rangle &= \text{Tr}(\hat{\rho}\hat{A}) = \int dx \langle x | \hat{\rho}\hat{A} | x \rangle \\ &= \iint dx dx' \rho(x, x') A(x', x) \end{aligned} \quad (2.12)$$

where $O(x, x') = \langle x | \hat{O} | x' \rangle$, \hat{O} is any operator.

Let y describe the coordinate of the rest of the universe. One can show that

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \iiint dx dx' dy A(x', x) \psi^*(x', y) \psi(x, y) \quad (2.13)$$

where $\psi(x, y) = \langle x | \langle y | \psi \rangle$ is the entire wave function.

Comparing eq. (2.12) with eq. (2.13), we obtain

$$\rho(x, x') = \int dy \psi(x, y) \psi^*(x', y) \quad (2.14)$$

Eq. (2.14) shows that the density matrix can be found from the knowledge of the entire wave function which implies that the density matrix contains all of the information from the rest of the universe which influences the system.

2.3 DENSITY MATRIX IN STATISTICAL MECHANICS [2]

In this section, we will make the general description of the density matrix in previous section more practical in the real nature by using the knowledge of canonical distribution in section 2.13.

Let the whole universe be composed of system and reservoir which is the rest of the universe. The density matrix now contains the information about reservoir that influences the system. If we impose the system is influenced by the (heat) reservoir (there is only the exchange of energy), then, by using canonical distribution, the reservoir influences the system in such a way that the probability that the system is in state $|i\rangle$ which is characterized by energy E_i is $w_i = e^{-\beta E_i} / Z$. By these reasons, we can choose the basis that diagonalizes the density operator as the energy eigen ket $|\varphi_n\rangle$. Hence, the form of density operator becomes

$$\begin{aligned} \hat{\rho} &= \sum_n w_n |\varphi_n\rangle \langle \varphi_n| \quad ; \quad w_n = e^{-\beta E_n} / Z \\ &= \frac{1}{Z} \sum_n e^{-\beta \hat{H}} |\varphi_n\rangle \langle \varphi_n| = \frac{e^{-\beta \hat{H}}}{Z} \end{aligned} \quad (2.15)$$

where

$$\begin{aligned} Z &= \sum_n e^{-\beta E_n} = \sum_n \langle \varphi_n | e^{-\beta \hat{H}} | \varphi_n \rangle \\ &= \text{Tr}(e^{-\beta \hat{H}}) \end{aligned} \quad (2.16)$$

From eq. (2.9), eq. (2.15) and eq. (2.16), the expectation value of any operator \hat{A} is

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho}\hat{A}) = \frac{\text{Tr}(\hat{A}e^{-\beta\hat{H}})}{\text{Tr}(e^{-\beta\hat{H}})} \quad (2.17)$$

Note that all of the result in this section can only be used in quantum mechanics since we have used the concept of bra, ket and operator. By this reason, the statistical mechanics which has just been shown above is called "quantum statistical mechanics". To understand more clearly why it is quantum, one should look at eq. (2.11). Eq. (2.11) can be written in the form

$$\begin{aligned} \langle \hat{A} \rangle &= \sum_i w_i \langle i | \hat{A} | i \rangle = \sum_i \sum_j a_j w_i w_{i \rightarrow j} \quad ; \quad w_{i \rightarrow j} = |\langle a_j | i \rangle|^2 \\ &= \sum_j a_j P_j \quad ; \quad P_j = \sum_i w_i w_{i \rightarrow j} \end{aligned} \quad (2.18)$$

where a_j and $|a_j\rangle$ are the eigen value and eigen vector of an operator \hat{A} respectively. Note that in this equation $w_i = e^{-\beta E_i} / Z$ and $|i\rangle$ is the energy eigen ket corresponding to eigen value E_i .

From eq. (2.18), one can see the probability that the system is in state $|a_j\rangle$ denoted by P_j depends on both w_i and $w_{i \rightarrow j}$ which are the probability due to the thermal fluctuation and quantum fluctuation respectively. So, it is clear that the expectation value of any operator \hat{A} can be calculated via the probability P_j which is composed of the effect from thermal and quantum behavior.

Notice that eq. (2.15) and eq. (2.17) can be obtained by using the general formalism of the density matrix in previous section. However instead of the use of general formalism of density matrix, we can also derive these equations by using basic probability theory and some of the basic knowledge in quantum theory as follows:

Let w_i be the probability that the system is in state $|i\rangle$. Let $w_{i \rightarrow j}$ be the transition probability from state $|i\rangle$ to state $|a_j\rangle$ i.e., the probability that the system is found in state $|a_j\rangle$ if initially it has been known in state $|i\rangle$. Since the event that the system is in state $|i\rangle$ and the event that the system changes from (initially known) state $|i\rangle$ to state $|a_j\rangle$ are independent to each other, the event that the system is in state $|i\rangle$ and then transition to state $|a_j\rangle$ is the successive event of these two independent events so the probability of

this successive event is the product of the probability of these two independent events i.e., $w_i w_{i \rightarrow j}$. From quantum mechanics, we know that $\langle i|i' \rangle = \delta_{ii'}$, so if the system is in state $|i\rangle$, it is not in state $|i'\rangle$ which imply that the event that the system is in state $|i\rangle$ and state $|i'\rangle, i' \neq i$ form the mutually exclusive event. Hence, the probability that the system is found in state $|a_j\rangle$ denoted by P_j is equal to the sum of the probability that the system is in state $|i\rangle$ and then transition to state $|a_j\rangle$ over all mutually exclusive events $|i\rangle$ i.e., $P_j = \sum_i w_i w_{i \rightarrow j}$. From probability theory, the expectation value of the random variable which is an operator \hat{A} in our case is $\langle \hat{A} \rangle = \sum_j a_j P_j = \sum_j \sum_i w_i w_{i \rightarrow j}$. From quantum theory, $w_{i \rightarrow j} = |\langle a_j | i \rangle|^2$ so $\langle \hat{A} \rangle = \sum_i \sum_j a_j w_i |\langle a_j | i \rangle|^2 = \sum_i w_i \langle i | \hat{A} | i \rangle$. In this section, $w_i = e^{-\beta E_i} / Z$ and $\hat{H} |i\rangle = E_i |i\rangle$ so $\langle \hat{A} \rangle = \sum_i \langle i | e^{-\beta E_i} \hat{A} | i \rangle / Z = \sum_i \langle i | e^{-\beta \hat{H}} \hat{A} | i \rangle / Z = \text{Tr}(\hat{A} e^{-\beta \hat{H}}) / \text{Tr}(e^{-\beta \hat{H}}) = \text{Tr}(\hat{\rho} \hat{A})$ where $\hat{\rho} = e^{-\beta \hat{H}} / Z$, $Z = \text{Tr}(e^{-\beta \hat{H}})$. These above results are identical to eq. (2.11), eq. (2.15), eq. (2.16), and eq. (2.17).

Now, from eq. (2.15) we define the "unnormalized density operator" $\hat{\rho}_U$ by $\hat{\rho}_U = e^{-\beta \hat{H}}$. "In place of $\hat{\rho}_U$ we will hereafter write $\hat{\rho}$ ". From eq. (2.16) and eq. (2.17), it is clear that if one knows $\hat{\rho}$ especially in position representation, $\rho(x, x') = \langle x | \hat{\rho} | x' \rangle$, the partition function (by eq. (2.16), $Z = \int \rho(x, x) dx$) and expectation of any operator can be found easily e.g., by eq. (2.12). So, the problem of quantum statistical mechanics now hinge on finding the density matrix. In order to find it, one should first find its equation of motion.

Considering the (unnormalized) density operator which we regard as a function of β , $\hat{\rho}(\beta) = e^{-\beta \hat{H}}$, it is easy to prove that

$$-\frac{\partial \hat{\rho}}{\partial \beta} = \hat{H} \hat{\rho} \quad \text{with initial condition} \quad \hat{\rho}(0) = 1 \quad (2.19)$$

We can write eq. (2.19) in the position representation as follows:

$$\frac{\partial \rho(x, x'; \beta)}{\partial \beta} = \hat{H}_x \rho(x, x'; \beta) \quad \text{with initial condition} \quad \rho(x, x'; 0) = \delta(x - x') \quad (2.20)$$

Here the subscript x on \hat{H}_x indicates that \hat{H}_x operates on x in $\rho(x, x'; \beta)$. One of the simple example of solving density matrix via eq. (2.20) which will be used in the next section is the density matrix of the one-dimensional free particle. The Hamiltonian is

$$\hat{H} = \frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (2.21)$$

Inserting eq. (2.21) into eq. (2.20), we get

$$\frac{\partial \rho(x, x'; \beta)}{\partial \beta} = \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \rho(x, x'; \beta) \quad \text{with the initial condition} \quad \rho(x, x'; 0) = \delta(x - x') \quad (2.22)$$

This is a diffusion-type equation so its solution can be written down readily:

$$\rho(x, x'; \beta) \equiv \rho_{free}(x, x'; \beta) = \sqrt{\frac{m}{2\pi \hbar^2 \beta}} \exp\left[-\left(\frac{m}{2\hbar^2 \beta}\right)(x - x')^2\right] \quad (2.23)$$

Although we have the differential equation to determine the density matrix, its solution with initial condition may not always be solved exactly. In the next section, we will review the path integration method for calculating the density matrix which is the very powerful method in many problems such as the quantum Brownian motion problem which will be discussed in the next chapter.

2.4 PATH INTEGRATION FORMULATION OF THE DENSITY MATRIX [2], [3]

The (unnormalized) density operator can be written as

$$\begin{aligned} \hat{\rho}(U) &= e^{-\hat{H}\epsilon/\hbar} e^{-\hat{H}\epsilon/\hbar} \dots e^{-\hat{H}\epsilon/\hbar} \quad ; \quad U = \beta\hbar \\ &= \hat{\rho}(\epsilon) \hat{\rho}(\epsilon) \dots \hat{\rho}(\epsilon) \quad (n \text{ factor}) \quad ; \quad n\epsilon = U \end{aligned} \quad (2.24)$$

In coordinate representation, eq (2.24) can be written in the form

$$\rho(x, x'; U) = \int \dots \int \rho(x, x_{n-1}; \epsilon) \rho(x_{n-1}, x_{n-2}; \epsilon) \dots \rho(x_1, x'; \epsilon) dx_1 \dots dx_{n-1} \quad (2.25)$$

Eq. (2.25) can be written symbolically as

$$\rho(x, x'; U) = \int_{x'}^x Dx(\tau) \Phi[x(\tau)] \quad (2.26)$$

where $\Phi[x(\tau)]$ and $Dx(\tau)$ is a functional of the path $x(\tau)$ and functional measure respectively which will be determined later. The integration eq. (2.26) is called the "path integration". We will discuss later why we use this name.

In order to find the forms of $\Phi[x(\tau)]$ and $Dx(\tau)$, one should know the form of $\rho(x_{n-1}, x_{n-2}; \epsilon)$ for each n and use eq. (2.25) to determine them. In general case of particle in any potential i.e., $\hat{H} = \hat{P}^2/2m + V(\hat{x})$, one can think that the density matrix

$\rho(x, x'; \varepsilon)$ will differ from $\rho_{free}(x, x'; \varepsilon)$ for small ε by a small correction due to the presence of the potential $V(x)$.

From perturbation theory of the density matrix [2], [3], the first order approximation gives

$$\begin{aligned} \rho(x, x'; \varepsilon) - \rho_{free}(x, x'; \varepsilon) &\equiv \delta \rho(x, x'; \varepsilon) \\ &\approx \int_{-\infty}^{\infty} dx'' \int_0^{\varepsilon} \rho_{free}(x, x''; \varepsilon - \tau) V(x'') \rho_{free}(x'', x'; \tau) \frac{d\tau}{\hbar} \end{aligned} \quad (2.27)$$

For low ε , because ρ_{free} is a very localized Gaussian, most of the contributions in the integral over x'' occur near $x'' = x_0$ where $x_0 = (\tau x + (\varepsilon - \tau)x')/\varepsilon$. So we can, for small ε , write eq. (2.27) as

$$\begin{aligned} \delta \rho(x, x'; \varepsilon) &\approx - \int_0^{\varepsilon} \frac{d\tau}{\hbar} V(x_0) \int_{-\infty}^{\infty} dx'' \rho_{free}(x, x''; \varepsilon - \tau) \rho_{free}(x'', x'; \tau) \\ &= - \int_0^{\varepsilon} \frac{d\tau}{\hbar} V(x_0) \rho_{free}(x, x'; \varepsilon) \end{aligned} \quad (2.28)$$

Now, if $x \approx x'$, x_0 is also close to x and $V(x_0)$ is constant over the range of integration. So, eq. (2.28) can be written as

$$\delta \rho(x, x'; \varepsilon) \approx - \frac{\varepsilon}{\hbar} V(x) \rho_{free}(x, x'; \varepsilon)$$

or

$$\begin{aligned} \rho(x, x'; \varepsilon) &\approx - \rho_{free}(x, x'; \varepsilon) \left[1 - V(x) \frac{\varepsilon}{\hbar} \right] \\ &\approx \rho_{free}(x, x'; \varepsilon) e^{-V(x)\varepsilon/\hbar} \end{aligned} \quad (2.29)$$

Inserting eq. (2.23) into eq. (2.29), we get

$$\rho(x, x'; \varepsilon) \approx \sqrt{\frac{m}{2\pi \hbar \varepsilon}} \exp \left[\frac{-m(x-x')^2}{2\hbar \varepsilon} - \frac{\varepsilon V(x)}{\hbar} \right] \quad (2.30)$$

Inserting eq. (2.30) into eq. (2.25), we obtain

$$\rho(x, x'; U) = \int_{x'}^x Dx(\tau) \exp \left\{ - \frac{1}{\hbar} \int_0^U \left[\frac{1}{2} m \dot{x}^2(\tau) + V(x(\tau)) \right] d\tau \right\} \quad (3.31)$$

where the functional measure $Dx(\tau) = (m/2\pi \hbar \varepsilon)^{n/2} dx_1 dx_2 \dots dx_{n-1}$. By comparing eq.

(2.31) with eq. (2.26), we get $\Phi[x(\tau)] = -(1/\hbar) \int_0^U [m\dot{x}^2(\tau)/2 + V(x(\tau))] d\tau$.

Notice that eq. (2.31) looks like the ordinary path integration in quantum mechanics [3]. So in order to make an interpretation of path integration in quantum statistical mechanics, we should compare the result in this section with the ordinary path integration and consider again how we can interpret it.

In quantum mechanics, the propagator $K(a, b; T)$, the probability amplitude of the particle starts from point a and reach point b within the time interval T , can be expressed in the form [3]

$$K(a, b; T) = \int_a^b Dx(t) e^{\frac{i}{\hbar} S[x(t)]} \quad (2.32)$$

where $S[x(t)] = \int_0^T L(x, \dot{x}, t) dt$ is called the "action" and $L(x, \dot{x}, t)$ is called the "Lagrangian" which is in the form (for velocity independent force field)

$$L(x, \dot{x}) = \frac{1}{2} m \dot{x}^2(t) - V(x(t)) \quad (2.33)$$

Another form of the propagator is [3]

$$K(a, b; T) = \sum_n \varphi_n^*(a) \varphi_n(b) e^{-\frac{i}{\hbar} E_n T} \quad (2.34)$$

where $\varphi_n(x)$ and E_n are the energy eigen function and corresponding energy eigen value respectively. Moreover, $K(a, b; T)$ satisfies the partial differential equation (Schrödinger equation for the kernel)

$$\hat{H}_a K(a, b; T) = i\hbar \frac{\partial}{\partial T} K(a, b; T) \quad (2.35)$$

where the subscript a on \hat{H}_a indicates that \hat{H}_a operates only on a in $K(a, b; T)$

In quantum statistical mechanics, the density matrix, by eq. (2.31), can be expressed in the form

$$\rho(x, x'; U) = \int_{x'}^x Dx(\tau) e^{-\frac{1}{\hbar} S^E[x(\tau)]} \quad (2.36)$$

where $S^E[x(\tau)] = \int_0^U L^E(x, \dot{x}, t) d\tau$ is called the "Euclidean action" and $L^E(x, \dot{x})$ is called the "Euclidean Lagrangian" which is in the form (for velocity independent force field)

$$L^E(x, \dot{x}) = \frac{1}{2} m \dot{x}^2(\tau) + V(x(\tau)) \quad (2.37)$$

Another form of the density matrix, like in eq. [2.34], can also be obtained by considering

$$\rho(x, x'; U) = \langle x | \hat{\rho} | x' \rangle = \sum_n e^{-\beta E_n} \langle x | \varphi_n \rangle \langle \varphi_n | x' \rangle = \sum_n \varphi_n^*(x') \varphi_n(x) e^{-\frac{E_n U}{\hbar}} \quad (2.38)$$

Moreover, like eq. (2.35), $\rho(x, x'; U)$ satisfy the partial differential equation, by eq. (2.20),

$$\hat{H}_x \rho(x, x'; U) = -\hbar \frac{\partial}{\partial U} \rho(x, x'; U) \quad (2.39)$$

Now, comparing eq. (2.34) with eq. (2.38) and eq. (2.35) with eq. (2.39), it is clear that these formulas in quantum mechanics coincide with the formulae in quantum statistical mechanics when we replace T by $-iU (= -i\beta \hbar)$. Moreover, $(i/\hbar)S[x(t)]$ coincides with $-(1/\hbar)S^E[x(\tau)]$ when the particle in quantum mechanics moves within the time interval $T = -iU$. In quantum mechanics, the path integration formalism of the propagator, eq. (2.32), can be interpreted as a "sum over all possible path" [3] since the functional measure $Dx(t)$ [3],[5] is composed of the integration over real line of each intermediate step, x_1, x_2, \dots, x_n (see fig. 2.1).

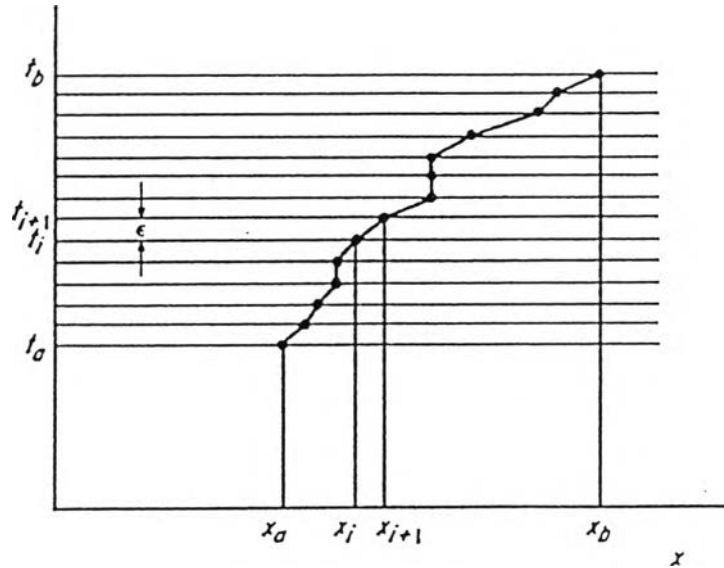


Fig. 2.1: The sum over all possible paths is defined as a limit, in which at first the path is specified by giving only its coordinate x at a large number of specified times separated by very small intervals ϵ . The path sum is then an integral over all these specific coordinates. Then to achieve the correct measure, the limit is taken as ϵ approach 0 (see ref. [3]).

So, by using those comparisons we have shown above, the path integration formalism of the density matrix can also be interpreted as a "sum over all possible path" (since the functional measure $Dx(t)$ also contains the integration of each intermediate step, x_1, x_2, \dots, x_n , see eqs. (2.25) and (2.31). This is the answer why eq. (2.26) is called the path integration.) but the particle, instead of moving within the real time interval, moving within the imaginary time interval. By these reasons, the path integration formalism of the density matrix is sometimes called the "imaginary time path integration" while the path integration formalism of the propagator is sometimes called the "real time path integration". Moreover, by using the connection between imaginary and real time path integration ($t = -i\tau$), the path integration formalism of the density matrix eq. (2.36) can also be derived in a different way (without using the perturbation theory) via a real time path integral formalism [3]. When looking at eq. (2.32) or eq. (2.36), one may ask: what is the main contribution path of the path integral? The answer is the path which is called the "classical path". Its corresponding action functional or Euclidean action functional is minimum which implies that $\delta S = 0$ or $\delta S^E = 0$ at this path. This answer comes from the fact that, first, in quantum mechanics, the integrand is $\exp(iS/\hbar)$ so many paths near the classical path make a constructive interference because there is, in the first order at least, no change in S among these paths while the other paths make a destructive interference, second, in quantum statistical mechanics, the integrand is $\exp(-S^E/\hbar)$ so the path which is far from classical path makes a large Euclidean action which implies that $\exp(-S^E/\hbar)$ is small due to a large exponential decay. However, the event that the classical path is a main contribution path will occur when the order of S or S^E is big comparing to \hbar (this is a situation which classical physics might be expected to work) otherwise other paths may become a contribution path too.

In standard classical mechanics [4], the minimization of action gives us that the classical path must be the path which obeys the Lagrange's equation and the rough pictorial of classical motion can be obtained by drawing the potential $V(x)$ with specific particle's total energy E . Similarly but not exactly the same for our case of quantum statistical mechanics, the system, instead of describing by the action, is described by the Euclidean action S^E . The classical path in this case is also defined as the path that

minimizes the Euclidean action i.e., $\delta S^E = 0$ and this minimization also provides that the classical path must satisfy the Lagrange's equation. The Lagrangian in this case is now the Euclidean Lagrangian which is, instead of $T - V$, equal to $T + V = T - (-V)$. Hence, the rough pictorial of classical motion can be obtained by drawing the "inverted potential" $-V(\mathbf{x})$ instead of $V(\mathbf{x})$ with specific particle's total energy $-E$ instead of E . There are many techniques [3], [5] which can be used to evaluate the path integration but the most conventional technique is the technique of expanding paths about the classical path. This technique is quite powerful because when expressing any path to be the classical path plus its deviation from this classical path, the original path integration will reduce to the simple form $F(T)\exp(-iS_{cl}/\hbar)$ or $F(U)\exp(-S_{cl}^E/\hbar)$, where S_{cl} and S_{cl}^E are the action and Euclidean action evaluated at the classical path respectively, when $F(T)$ or $F(U)$ are still the path integration but all paths are the close path starting and ending at the same point which is equal to zero. Moreover, $F(T)$ or $F(U)$ consists of only the quadratic term in the exponent of the integrand. By these reasons, $F(T)$ or $F(U)$ can be easily evaluated by using Fourier series [3].

Now, let us summarize the main ideas in this section. The density matrix can be calculated by using the path integration formalism via eq. (2.36). This density matrix can be interpreted as the propagator of particle moving within the imaginary time interval. The main contribution of the path integral comes from the classical path which is defined as the path corresponding to the minimum Euclidean action. The classical motion is identical to the motion of particle in the inverted potential with minus of the total energy.

Before ending this chapter, it is worth to note that the reader should be careful in making interpretation of path integration in quantum statistical mechanics (imaginary time path integration). In the real nature of statistical system, there exists no real particle moving along this path or that path within the given time interval, the interpretation was made by using the analogy to quantum mechanics which surely has the real moving particle. This interpretation has been made in order to help someone understand the abstract statistical problem more pictorial concerning the motion of particle in the sense of classical physics.