Chapter 2
Statistical Mechanics

This chapter is devoted to a review of statistical mechanics putting the emphasis on the path integral approach to the subject. Our treatment is rather sketchy and the reader is invited to consult the book by Feynman [6] and the original papers cited for more details.

2.1 Quantum Statistical Mechanics

The main purpose of this chapter is to give a short introduction to the path integrals for statistical mechanics and to consider this formulation for identical-particle systems. Normally, in the framework of quantum mechanics via path integrals, we consider the system going from one state to another, say a particle at the point x_1 going to x_2, and find the transition probability amplitude. In statistical mechanics we consider the quantum mechanical states in thermal equilibrium at some temperature T. The probability of finding the system in the state of energy E is associated with the factor $e^{-\beta E}$, the Boltzmann factor, where $\beta = 1/\left(k_B T\right)$. This factor acts as a weighting function for the determination of any observable. For example the probability of finding a system in the state with energy E_a can be written as

$$P_{E_a} = \frac{1}{Z} e^{-\beta E_a} \tag{2.1}$$

where $Z = \sum_i e^{-\beta E_i}$ is the partition function which serves as a normalization factor. From the knowledge of the partition function we can derive all thermodynamic properties of the system in thermal equilibrium. For example, if we want to know the probability of finding the system at the point x, we first find the complete set of wave functions of the system $\{\phi_i(x)\}$ and then we can write the probability of finding the system at the position x as

$$P(x) = \frac{1}{Z}\sum_i \phi_i^*(x)\,\phi_i(x)\,e^{-\beta E_i}. \tag{2.2}$$

The expectation value of the observable A can be calculated from

$$\langle A\rangle = \frac{1}{Z}\sum_i A_i e^{-\beta E_i} = \frac{1}{Z}\sum_i \int \phi_i^*(x)\,A(x)\,\phi_i(x)\,e^{-\beta E_i}dx \tag{2.3}$$

where $A_i = \int \phi_i^*(x)\,A(x)\,\phi_i(x)\,dx$ is the mean value of A in the state i. If we define the function

$$\rho(x, x') = \sum_i \phi_i^*(x')\,\phi_i(x)\,e^{-\beta E_i} \tag{2.4}$$

called the density matrix of the quantum statistical system, the expectation value of the observable A and the partition function can be respectively written as

$$\langle A\rangle = \frac{1}{Z}\int \rho(x, x)\,A(x)\,dx = \frac{1}{Z}\mathbf{Tr}(\rho A) \tag{2.5}$$

and

$$Z = \int \rho(x, x)\,dx = \mathbf{Tr}(\rho), \tag{2.6}$$

where $\mathbf{Tr}(\rho)$ represents the trace of ρ. The general problem of quantum statistical mechanics is to determine the density matrix. Once we know this function all the thermodynamical quantities of the system can be derived.

2.2 Path Integral Evaluation of the Density Matrix

From the formulation of path integration for quantum mechanics, the main quantity of interest is the path integral propagator

$$K\left(x',T|x,0\right)=\sum_{i}\phi_i^*\left(x'\right)\phi_i\left(x\right)\exp\left[-\frac{i}{\hbar}E_iT\right] \tag{2.7}$$

describing a quantum system going from $(x,0)$ to (x',T). Notice that this is resemble to the density matrix we derived in the previous section, we can see that if we replace the time interval T by the inverse temperature factor $-i\hbar\beta$ we can obtain the expression for the density matrix. Mathematically speaking we do the analytic continuation of the variable t in the complex plane. Or we can write explicitly in the path integral form as

$$\begin{aligned} K\left(x',T|x,0\right) &= \int_{x(0)}^{x'(T)}\mathcal{D}\left[x\left(t\right)\right]\exp\left[\frac{i}{\hbar}\int_0^T Ldt\right] \\ &= \int_{x(0)}^{x'(T)}\mathcal{D}\left[x\left(t\right)\right]\exp\left[\frac{i}{\hbar}S\right]. \end{aligned} \tag{2.8}$$

After performing analytic continuation $T\rightarrow -i\hbar\beta$, we have

$$\begin{aligned} \rho\left(x',-i\hbar\beta|x,0\right) &= \int_{x(0)}^{x'(\beta\hbar)}\mathcal{D}\left[x\left(\tau\right)\right]\exp\left[-\frac{1}{\hbar}\int_0^{\beta\hbar}\mathcal{L}d\tau\right] \\ &= \int_{x(0)}^{x'(\beta\hbar)}\mathcal{D}\left[x\left(\tau\right)\right]\exp\left[-\frac{\mathcal{S}}{\hbar}\right] \end{aligned} \tag{2.9}$$

where $\mathcal{S}$ and $\mathcal{L}$ denote the action and Lagrangian respectively in the new variable and $\tau\equiv it$ is called the imaginary time. Note that we treat τ as a real variable and notice that $\dot{x}=idx/d\tau$ so the Lagrangian is modified to $\mathcal{L}=T+V$ with $T=md^2x/d\tau^2$. Physically, the imaginary time is nothing more than a parameter characterizing the thermodynamical systems like what the real time does in quantum mechanics. Time in quantum mechanics parametrizes the evolution of a system and the imaginary time or the inverse temperature characterizes the system at equilibrium at each temperature. Sometimes this imaginary time is called the Euclidean time because when we consider the line element of the four-dimension space-time (the Minkowski space) which can be written $ds^2 = -(cdt)^2 + d\vec{r}^2$, if we work in the imaginary-time formulation the line element becomes $ds^2 = (cd\tau)^2 + d\vec{r}^2$ as if the space-time is Euclidean. The formulation of path integrals in Euclidean space is very useful in Quantum Field Theory.

We can now picturize this formulation physically. We can see that the integrand of the path integral is in the form of exponential decays. The "sum-over-all-paths" is the summation of the probability amplitudes (having the form of the exponential of the action) associated with all possible paths connecting x to x'. Hence, the path that makes the action very large has a very small contribution to the sum. From the least action principle we know that the main contribution to the sum-over-all-paths is from the path that makes the action minimum, which is called the classical path. The small fluctuation paths around this classical path also give significant contributions to the path integral. The path in this context is the path parametrized by the imaginary time and the kinetic term in the Lagrangian is not a physical one.

So now we can say that our problem is to find the density matrix in the framework of imaginary time path integrals. In the real time path integral there is an important property of the propagator, called the "group property,"

$$K(x_3, T_2 + T_1 | x_1, 0) = \int_{-\infty}^{\infty} K(x_3, T_2 | x_2, 0)\, K(x_2, T_1 | x_1, 0)\, dx_2. \tag{2.10}$$

We can see that this property is still valid in its imaginary time counterpart but we call it the "semi-group" property due to the lack of inverse of the density matrix.

2.3 Systems of Many Particles

We now consider the systems with several variables. We treat the system of particles as an identical-particle system with the particles being either distinguishable or indistinguishable. In each case we have to apply different way of counting due to the symmetry corresponding to each type of statistics. We can write the Lagrangian for a system of N particles in general as

$$\mathcal{L} = \sum_{i=1}^{N} \left(\dot{\vec{r}}_i^{\,2} + V_{ext}\left(\vec{r}_i\right) + \frac{1}{2} \sum_{j \neq i}^{N} V_{int}\left(\vec{r}_i - \vec{r}_j\right) \right) \tag{2.11}$$

where $V_{ext}\left(\vec{r}_i\right)$ is an external potential acting on the particle i and $V_{int}\left(\vec{r}_i - \vec{r}_j\right)$ represents the interaction between particles i and j. Actually the interaction terms can be multinary instead of binary as written above. However as the path integration calculations rely mostly on the classical solutions of the Euler-Lagrange equations, the binary interaction is easy to deal with but it is very difficult to solve the many-body problem analytically. The density matrix associated with this Lagrangian is

$$\rho\left(\left\{x'\right\}, \beta \middle| \left\{x\right\}, 0\right) = \int_{\{x(0)\}}^{\{x'(\beta)\}} \mathcal{D}^N \left[\left\{x\left(\tau\right)\right\}\right] \exp\left[- \int_0^\beta \mathcal{L} d\tau \right] \tag{2.12}$$

where $\{x\} \equiv \{x_1, x_2, ..., x_N\}$ denotes the collection of N coordinates of the system and the path integral measures $\mathcal{D}^N\left[\left\{x\left(\tau\right)\right\}\right] = \mathcal{D}\left[x_1\left(\tau\right)\right] \mathcal{D}\left[x_2\left(\tau\right)\right] \cdots \mathcal{D}\left[x_N\left(\tau\right)\right]$. We set $m = \hbar = 1$ for simplicity. We write here in one dimension but the generalization to the three-dimensional case is obvious. Our next step is to consider the many-body density matrix in three categories:

1. Distinguishable particle case (Maxwell-Boltzman statistics)

$$\rho_D\left(\{x'\},\beta|\{x\},0\right)=\sum_i \phi_i\left(\{x'\}\right)\phi_i\left(\{x\}\right)e^{-\beta E_i} \tag{2.13}$$

2. Symmetric case (Bose-Einstein statistics)

$$\rho_{sym}\left(\{x'\},\beta|\{x\},0\right)=\frac{1}{N!}\sum_P\sum_i \phi_i^*\left(\{Px'\}\right)\phi_i\left(\{x\}\right)e^{-\beta E_i} \tag{2.14}$$

3. Anti-symmetric case (Fermi-Dirac statistics)

$$\rho_{antisym}\left(\{x'\},\beta|\{x\},0\right)=\frac{1}{N!}\sum_P(-1)^P\sum_i \phi_i^*\left(\{Px'\}\right)\phi_i\left(\{x\}\right)e^{-\beta E_i} \tag{2.15}$$

where $\sum_P$ means the sum over all permutations. $\{Px\}$ is a permutation of x_i with respect to $\{x\}$. We can see that $\phi_i^*\left(\{Px'\}\right)\phi_i\left(\{Px\}\right)=\phi_i^*\left(\{x'\}\right)\phi_i\left(\{x\}\right)$ since $P^2=1$. For the last two cases, we can express the density matrix in a general form as

$$\rho\left(\{x'\},\beta|\{x\},0\right)=\frac{1}{N!}\sum_P \xi^P\rho_D\left(\{Px'\},\beta|\{x\},0\right) \tag{2.16}$$

where $\xi=1$ for Bose-Einstein statistics, $\xi=-1$ for Fermi-Dirac case.

The problem is how to do the sum over all permutations. We know from group theory, particularly the theory of permutation group, that any permutation can be broken into cycles. Consider, for example, a cycle of length 8 which can be symbolically represented by (12345678). Let us consider one particular case of the permutation $P_1=(15624387)$ which means $(1\rightarrow 1)$, $(2\rightarrow 5)$, $(3\rightarrow 6)$, $(4\rightarrow 2)$, $(5\rightarrow 4)$, $(6\rightarrow 3)$, $(7\rightarrow 8)$ and $(8\rightarrow 7)$. This permutation can be decomposed as $(1)(254)(36)(78)$ which means that the figures in the parentheses are permuted cyclically. Then we say that P_1 is broken into one cycles of length 1, one cycle of length 3 and two cycles of length 2.

We now show that the knowledge about the permutation group would simplify the problem if the Lagrangian takes the form of that of N non-interacting particles. In such case, the many-body wave function is simply the product of single-particle wave functions and the N-particle density matrix can be written as a product of single-particle density matrices. The important quantity when we want to find the thermodynamic quantity is the partition function which can be derived by taking the trace of the density matrix, or equivalently, by setting $\{x'\} = \{x\}$ and integrating over $x_1, x_2, ..., x_N$:

$$Z_N = \frac{1}{N!}\sum_P \xi^P \left(\int \rho_D \left(\{Px\}, \beta | \{x\}, 0\right) dx_1 dx_2 \cdots dx_N \right). \tag{2.17}$$

According to the cyclic decomposition described above, we can write the partition function as (for details see [6])

$$Z_N = \frac{1}{N!}\sum_{M_1, M_2, .., M_N} \left\{ \frac{N!}{\left(\prod_\gamma (M_\gamma!)\, \gamma^{M_\gamma}\right)} \prod_\gamma \left(Z_1 (x, \gamma\beta | x, 0)\right)^{M_\gamma} \right\} \tag{2.18}$$

where M_γ is the number of the cycles of length γ, the summations are subject to the constraint $\sum_{\gamma=1}^{N} \gamma M_\gamma = N$ and $Z_1 (x', \gamma\beta | x, 0)$ is a single-particle partition function with immaginary-time interval $\gamma\beta$ (in the other words, at the temperature $T = 1/(\gamma\beta k_B)$ obtained from the single-particle density matrices as

$$\begin{aligned} Z_1 (x', \gamma\beta | x, 0) &= \int dx dx_1 dx_2 ... dx_{\gamma-1} \rho_1 (x, \beta | x_1, 0)\, \rho_1 (x_1, \beta | x_2, 0) \cdots \rho_1 (x_{\gamma-1}, \beta | x, 0) \\ &= \int dx \rho_1 (x, \gamma\beta | x, 0) . \end{aligned} \tag{2.19}$$

In deriving the above result we have used the semigroup property of the density matrix, Eq. (2.10). The factor $N!/\left(\prod_\gamma (M_\gamma!)\, \gamma^{M_\gamma}\right)$ is the number of distinct permutations of the $\{M_\gamma\}$ configuration. In the later chapters we will see that this expression makes us correctly count the possible configurations. Rewrite the partition function in Eq. (2.18) as

$$Z_N = \sum_{M_1,M_2,..,M_N} \left\{ \prod_{\gamma} \frac{\left(Z_1\left(\gamma\beta\right)\right)^{M_\gamma}}{M_\gamma! \nu^{M_\gamma}} \right\}. \tag{2.20}$$

The sum $\sum_{M_1,M_2,..,M_N}$ is not practical to evaluate since there are various configurations of partitioning of the cycles and also we have the constraint $\sum_{\gamma=1}^{N} \gamma M_\gamma = N$. It is therefore more convenient to use the grand canonical ensemble in which the number of particles in the system can be varied. In this ensemble, the main object of interest is the grand partition function

$$\begin{aligned} \mathbb{Z} &= \sum_{N=0}^{\infty} e^{\mu N} Z_N \\ &= \sum_{N=0}^{\infty} \sum_{M_1,M_2,..,M_N} \left\{ \prod_{\gamma} \frac{\left(Z_1\left(\gamma\beta\right)\right)^{M_\gamma}}{M_\gamma! \nu^{M_\gamma}} \left(e^{\mu}\right)^{\gamma M_\gamma} \right\} \end{aligned} \tag{2.21}$$

where we have defined $Z_0 = 1$ and the chemical potential μ has been introduced to account for the change of the energy of the system when the particles are added or removed. Since $\sum_{N=0}^{\infty} \sum_{M_1,M_2,..,M_N} = \sum_{M_1=0}^{\infty} \sum_{M_2=0}^{\infty} \cdots \sum_{M_i=0}^{\infty} \cdots$, we can further simplify the above expression as

$$\begin{aligned} \mathbb{Z} &= \sum_{M_1=0}^{\infty} \sum_{M_2=0}^{\infty} \cdots \sum_{M_i=0}^{\infty} \cdots \left\{ \prod_{\gamma} \frac{\left(Z_1\left(\gamma\beta\right)\right)^{M_\gamma}}{M_\gamma! \nu^{M_\gamma}} \left(e^{\mu}\right)^{\gamma M_\gamma} \right\} \\ &= \prod_{\gamma} \left\{ \sum_{M_\gamma=0}^{\infty} \frac{\left(Z_1\left(\gamma\beta\right)\left(e^{\mu}\right)^{\gamma}/\gamma\right)^{M_\gamma}}{M_\gamma!} \right\} \\ &= \prod_{\gamma} \exp\left[\frac{Z_1\left(\gamma\beta\right)\left(e^{\mu}\right)^{\gamma}}{\gamma} \right]. \end{aligned} \tag{2.22}$$

Notice that this cyclic decomposition is valid only in the case that the N-particle density matrix can be written as a product of single-particle density matrices. To give more insights into this formulation, we give an example in the next section.

2.4 Model of Coupled Identical Oscillators

Brosens et al. [7,8] consider the system of identical particles in harmonic potential interacting with harmonic interactions,

$$\mathcal{L} = \sum_{i=1}^{N} \frac{1}{2}\dot{\vec{r}}_i^2 + \frac{1}{2}\sum_{i=1}^{N} \Omega^2 \vec{r}_i^2 + \frac{\omega^2}{4}\sum_{i=1}^{N}\sum_{j=1}^{N} (\vec{r}_i - \vec{r}_j)^2 \tag{2.23}$$

As pointed out in the last section, to do the cyclic decomposition we need to write the N-particle density matrix in the form of a product of single-particle density matrices. Hence introducing the center of mass and the relative coordinates,

$$\vec{R} = \frac{1}{N}\sum_{i=1}^{N} \vec{r}_i \quad \text{and} \quad \vec{u}_i = \vec{r}_i - \vec{R}, \tag{2.24}$$

then the Lagrangian is modified to

$$\mathcal{L} = \frac{1}{2}N\dot{\vec{R}}^2 + \frac{1}{2}\Omega^2 N \vec{R}^2 + \sum_{i=1}^{N} \frac{1}{2}\dot{\vec{u}}_i^2 + \frac{1}{2}w^2 \sum_{i=1}^{N} \vec{u}_i^2 \tag{2.25}$$

where $w^2 = \Omega^2 - N\omega^2$. Although the above Lagrangian takes the form of the uncoupled harmonic oscillators, complications arise as we notice that the coordinates $\vec{u}_i$ are not independent: they must satisfy the constraint $\sum_{i=1}^{N} \vec{u}_i = 0$ which severely constrains the range of integration in the path integral. The way to solve this problem is to integrate over $\vec{R}$ and $\vec{u}_i$'s and then enforce the constraint via the insertion of the delta function, $\delta(\sum_{i=1}^{N} \vec{u}_i)$, in the path integral. The result is

$$\rho_D\left(\vec{r}', \beta | \vec{r}, 0\right) = \frac{\rho\left(\sqrt{N}\vec{R}', \beta | \sqrt{N}\vec{R}, 0\right)_\Omega}{\rho\left(\sqrt{N}\vec{R}', \beta | \sqrt{N}\vec{R}, 0\right)_w} \prod_{i=1}^{N} \rho\left(\vec{r}', \beta | \vec{r}, 0\right)_w \tag{2.26}$$

where, for example, $\rho\left(\sqrt{N}\vec{R}', \beta | \sqrt{N}\vec{R}, 0\right)_\Omega$ represents the density matrix of a particle with coordinate $\sqrt{N}\vec{R}$ in a harmonic potential of frequency Ω. The reader is invited to see the paper by Brosens et al. [7] for more details. By this way, the cyclic decomposition can be done within this model. As we will see in the next chapter, the approximate density matrix for BEC cannot be decoupled in this way and we need to find other method to decompose the permutation sum.