

CHAPTER 2

Statistical Mechanics

In this Chapter, we shall review the partition function and the density of matrices from Ref. [10]. Since these quantities were the key principle represented in statistical mechanics, and is related to statistical and quantum quantities, we shall explain this quantities in detail as a basis for the following Chapter.

2.1 The Partition Function

The key principle of statistical mechanics is as follows: If an equilibrium system can be in one of N states, then the probability of the system having energy E_n is $(1/Z)e^{-E_n/kT}$, where

$$Z = \sum_{n=1}^N e^{-E_n/kT}, \quad (2.1)$$

k = Boltzmann's constant, and T =absolute temperature. Z is called the *partition function*. If we take $|i\rangle$ as a state with energy E_i and A as a quantum-mechanical operator for a physical observable, then the expected value of the observable is

$$\langle A \rangle = \frac{1}{Z} \sum_{|i\rangle} \langle i|A|i\rangle e^{-E_i/kT}. \quad (2.2)$$

When Eq. (2.1) is solved then all thermodynamics properties can be found. We define F , the Helmholtz free energy, so that

$$Z \equiv e^{-F/kT}, \quad (2.3)$$

$$F = -kT \ln Z, \quad (2.4)$$

and we can define S , the entropy, as

$$S = -k \sum_n P_n \ln P_n \quad (2.5)$$

where P_n is the probability which is $(1/Z)e^{-E_n/kT}$. So we relate Eq. (2.5) with Eq. (2.4), it can be seen that

$$S = -\left(\frac{\partial F}{\partial T}\right). \quad (2.6)$$

When taking into account the pressure p and the average energy U , we get

$$p = -\sum_n P_n \frac{\partial E_n}{\partial V} = -\left(\frac{\partial F}{\partial V}\right)_T, \quad (2.7)$$

$$U = \frac{1}{Z} \sum_n E_n e^{-E_n/kT} = \frac{\partial}{\partial(1/T)} \frac{F}{T}. \quad (2.8)$$

Using Eq. (2.6) to rearrange Eq. (2.8), we get

$$U = F + TS. \quad (2.9)$$

Eq. (2.4) holds only at equilibrium, where F is defined. If we have a system that is a combination of several independent subsystems, the total energy of the subsystems is

$$F = -kT \ln \sum_{n_i} e^{-\beta \sum_i E_{n_i}} = -kT \ln \prod_i (\sum_{n_i} e^{-\beta E_{n_i}}) = -kT \sum_i [\ln \sum_{n_i} e^{-\beta E_{n_i}}] = \sum_i F_i.$$

The free energy of the whole system is the sum of the free energies of its noninteracting parts. Consider a system of harmonic oscillators in thermal equilibrium. The partition function Z , free energy F , and average energy U of the system of oscillators can be found as follows: The oscillators do not interact with each other. Since each oscillator is independent, one can find F_i of the i th oscillator. If the systems has M oscillators then $F = \sum_{i=1}^M F_i$. We have the i th energy as $E_{n_i} = \hbar\omega_i(n_i + 1/2)$. The i th partition function, free energy and average energy of the system are

$$Z_i = \sum_n e^{-\hbar\omega_i(n+1/2)/kT} = \frac{e^{-\hbar\omega_i/2kT}}{1 - e^{-\hbar\omega_i/2kT}}, \quad (2.10)$$

$$F_i = \frac{\hbar\omega_i}{2} + kT \ln(1 - e^{-\hbar\omega_i/kT}), \quad (2.11)$$

$$U_i = \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\hbar\omega_i/kT} - 1}. \quad (2.12)$$

That is, the total free energy and average energy of the system of oscillators can be found as $\sum_i^M F_i$ and $\sum_i^M U_i$, respectively.

2.2 Density Matrices

In a quantum-mechanical problem, we can divide the universe into two parts. Let x describe the coordinates of the system with a complete set of orthogonal wave

functions $\phi_i(x)$. And let y describe the coordinate of the rest of the universe with the complete set of orthogonal wave functions $\theta_i(y)$. The general wave function $\psi(x, y)$ can be written as $\sum_i C_i(y)\phi_i(x)$. At this point we will convert to Dirac's notation as $\phi_i(x) = \langle x|\phi_i\rangle$ and $\theta_i(y) = \langle y|\theta_i\rangle$. We can obtain the wave function by taking $C_i(y) = \sum_j C_{ij}\langle y|\theta_j\rangle$. The most general wave function can be written

$$|\psi\rangle = \sum_{ij} C_{ij}|\phi_i\rangle|\theta_j\rangle, \quad (2.13)$$

$$\psi(x, y) = \langle y|\langle x|\psi\rangle = \sum_{ij} C_{ij}\langle x|\phi_i\rangle\langle y|\theta_j\rangle. \quad (2.14)$$

Now let A be an operator that acts only on the system that is to say, A does not act on the $|\theta_j\rangle$. When A acts on product states we really mean $A|a\rangle|b\rangle \equiv (A|a\rangle)|b\rangle$. In such a case, A equals $\sum_{ii'} A_{ii'}|\phi_i\rangle|\theta_j\rangle\langle\theta_j|\langle\phi_{i'}|$, but does not equal $\sum_{ii'} A_{ii'}|\phi_i\rangle\langle\phi_{i'}|$. Then

$$\langle A\rangle = \sum_{ij i' j'} C_{ij}^* C_{i' j'} \langle\theta_j|\langle\phi_i|A|\phi_{i'}\rangle|\theta_{j'}\rangle = \sum_{ii'} \langle\phi_i|A|\phi_{i'}\rangle \rho_{ii'} \quad (2.15)$$

where

$$\rho_{ii'} = \sum_j C_{ij}^* C_{i' j'} \quad (2.16)$$

is defined as a density matrix. We define the operator ρ to be such that $\rho_{ii'} = \langle\phi_{i'}|\rho|\phi_i\rangle$. ρ operates only on the system described by x . That is,

$$\langle\psi|A|\psi\rangle = \sum_i \langle\phi_i|A \sum_{i'} |\phi_{i'}\rangle\langle\phi_{i'}|\rho|\phi_i\rangle = \sum_i \langle\phi_i|A\rho|\phi_i\rangle = Tr \rho A \quad (2.17)$$

where we have used the result by the completeness arguments $\sum_{i'} |\phi_{i'}\rangle\langle\phi_{i'}| = 1$. From Eq. (2.16), it is obvious that ρ is hermitian. Therefore it can be diagonalized with a complete orthonormal set of eigenvectors $|i\rangle$ and real eigenvalues w_i ,

$$\rho = \sum_i w_i |i\rangle\langle i|. \quad (2.18)$$

From Eq. (2.17), if we let A be 1, we obtain $\sum_i w_i = \text{Tr } \rho = 1$ and letting A be $|i\rangle\langle i'|$ we have that $w_{i'} = \sum_j |(\langle i'|\langle\theta_j|\psi\rangle)|^2 \geq 0$. Therefore, $w_i \geq 0$ and $\sum_i w_i = 1$.

We now consider the concept of a density matrix independent of the preceding motivation. Let us reformulate quantum mechanics. Any system is described by a density matrix ρ , where ρ is of the form $\sum_i w_i |i\rangle\langle i|$ and the set $|i\rangle$ is a complete orthonormal set of vectors, $w_i \geq 0$, $\sum_i w_i = 1$. Given an operator A , the expectation of A is given by $\text{Tr } \rho A$. Notice that

$$\langle A \rangle = \text{Tr } \rho A = \sum_{i'} \langle i' | \rho A | i' \rangle = \sum_{i'} w_i \langle i' | i \rangle \langle i | A | i' \rangle = \sum_i w_i \langle i | A | i \rangle. \quad (2.19)$$

Since $\langle i | A | i \rangle$ is the expectation value of A in the state $|i\rangle$, it is obvious that we can interpret the w_i as the probability that the system is in state i . In the x -representation we write

$$\langle A \rangle = \text{Tr } \rho A = \int dx \langle x | \rho A | x \rangle, \quad (2.20)$$

$$\langle x | \rho A | x \rangle = \int dx' \langle x | \rho | x' \rangle \langle x' | A | x \rangle = \int dx' \rho(x, x') A(x', x)$$

where $\rho(x, x') = \langle x | \rho | x' \rangle$ and $A(x', x) = \langle x' | A | x \rangle$. Then,

$$\langle A \rangle = \int dx dx' \rho(x, x') A(x', x). \quad (2.21)$$

Considering again the problem of a system plus the rest of the universe, we can easily show that

$$\langle A \rangle = \int \psi^*(x', y) A(x', x) \psi(x, y) dx dx' dy.$$

We see that in this case

$$\rho(x, x') = \int \psi(x, y) \psi^*(x', y) dy. \quad (2.22)$$

We split the universe into two parts, we see that pure states are not general enough to describe a quantum mechanical system that does not include the whole universe. It is unknown whether or not the universe is in a pure state. To reformulate quantum mechanics in terms of the more general density matrices, it would be appropriate next to find the equation of motion of ρ .

Alternatively, from Eq. (2.18) considering the coordinate representation of ρ we get

$$\rho(x, x') = \sum_i \frac{1}{Z} e^{-\beta E_i} \phi_i(x) \phi_i^*(x'). \quad (2.23)$$

From Eq. (2.23) if we consider $\phi_i(x)$ in orthonormal set, we have that

$$\rho(x, x') = \sum_i \phi_i(x) \phi_i^*(x') e^{-\beta E_i}. \quad (2.24)$$

Considering in energy representation as

$$\rho = \frac{1}{Z} \sum_n e^{-\beta H} |\phi_n\rangle \langle \phi_n| = \frac{e^{-\beta H}}{Z} \quad (2.25)$$

where H is the Hamiltonian of the system and $Z = \sum_n e^{-\beta E_n} = \text{Tr} e^{-\beta H}$, we obtain

$$\rho = \frac{e^{-\beta H}}{\text{Tr} e^{-\beta H}}. \quad (2.26)$$

In our study, we assume the statistical mechanic holds for the situation in cases. In the next Chapter, we will show that the density matrix can be represented in terms of Feynman path integral.