Chapter 1

Statistical Ensembles

1.1 Principle of statistical physics and ensembles

1.1.1 Partial information to partial result

Statistical systems are complex systems. The systems are so complex that we cannot obtain all the information to completely characterize the systems. For example, a liter of gas may contain $10^{22}$ atoms. To completely characterize such a system (or more precisely, a state of such a system), we need to known the three components of the velocity for each atoms and the three components of the position for each atoms. It is impossible to obtain $6 \times 10^{22}$ real numbers to completely characterize the gas.

However, not knowing all the information needed to characterize gas does not prevented us to develop a theory of gas. This is because we are only interested in some average properties of gas such as the pressure, volume, temperature. Those properties do not depend on every little details of each atoms. Not knowing every thing about the atoms does not prevent us from calculating those properties. This is the kind of problems in statistical physics. In statistical physics we try to understand the properties of a complex system without know all the information of the systems. This is possible since the properties that we are interested in do not depend on the all details of the system.

1.1.2 All possible states appear with an equal probability

In statistical physics there is only one principle: All possible states appear with an equal probability. Let us explain what do we mean by the above statement. Suppose we know certain quantities, such as pressure, total energy, etc, of a complex systems. But those quantities do not characterize the system completely. This means that the system has a number of states for which those quantities take the same values. Thus even after knowing the values of those quantities, we still do not know, among those possible states, which state the system is actually in. Then according to the principle of statistical physical, we say all the possible states are equally likely.

1.1.3 Time average and ensemble average

But the system can only be in one state at a given time. What do we mean by “all the possible states are equally likely”? There are two points of view. In the first point of view, we may imagine we have many copies of the system, all characterized by the same set of quantities, such as total energy, pressure, etc. But each copy may be in a different possible state. Then “equally likely” means that each possible
state appear the same number of times among the copies of the system. The copies of the system is called ensemble. We have to have an ensemble to even define the probabilities. Under the first interpretation, statistical physics is a science that deal with ensembles, rather than individual systems.

The second point of view only apply to the situation where the environment of the system is independent of time. In this case we interpret “equally likely” as that all the possible states appear for the same amount of time during a long period of time. The second point of view is related to the first point of view if we view the system at different times as the different copies of the system.

The two points of view may not be equivalent. The two points of view are equivalent only when the system can visit all the possible states, many times, during a long period of time. This is the ergodicity hypothesis.

Not all systems are ergodic. For a non-ergodic system, statistical physics only apply to its ensemble. For an ergodic system, statistical physics also apply to the time average of the system.

1.2 Microcanonical ensemble

A microcanonical ensemble is an ensemble formed by isolated systems. All the systems in the ensemble have the same energy (and possibly some other properties). Here by “same energy” we really mean that all systems has an energy which lies within a small window between $E$ and $E + \Delta E$.

1.2.1 Number of states and entropy

Let us first study a simple example: $N$ spins in magnetic field. The energy for an up-spin is $E^\uparrow = \epsilon_0/2$ and for a down-spin $E^\downarrow = -\epsilon_0/2$.

We like to ask: How many states are there with a total energy $E$?

Since the total energy is given by $E = M\frac{\epsilon_0}{2} - (N - M)\frac{\epsilon_0}{2}$, where $M$ is the number of up-spin. So the states with a total energy $E$ are the states with $M$ up-spins. But how many states are there with $M = \frac{E}{\epsilon_0} + \frac{N}{2}$ up-spins? The answer is $C^M_N = \frac{N!}{M!(N-M)!}$. (Here $C^M_N$ is the number of ways to pick $M$ objects from $N$ objects.) So the number of states with a total energy $E$ is

$$\Gamma(E) = C^E_N + \frac{N}{2}$$

After obtain the number of states as a function of total energy $E$, we can define the entropy of the system: the entropy is $k_B$ time the log of the number of states:

$$S(E) = k_B \ln \Gamma(E), \quad (1.2.1)$$

where $k_B = 1.3807 \times 10^{-16}$erg/K = 8.617343(15) $\times$ $10^{-5}$eV/K is the Boltzmann constant. (The Boltzmann constant is conversion factor between energy and temperature: 1K = 1.380710$^{-16}$erg = 8.617343(15) $\times$ $10^{-5}$eV. Or 1eV = 11605K. We will introduce the definition of temperature shortly.)

For a microcanonical ensemble, entropy a function of energy $E$. So for our $N$-spin system, the entropy is

$$S(E) = k_B \ln C^E_N + \frac{N}{2} \quad (1.2.2)$$

To calculate $\ln C^M_N$, we can use the Stirling’s approximation

$$\ln(n!) = n \ln n - n + \frac{1}{2} \ln(2\pi n) + O(1/n) \quad (1.2.3)$$
Thus (see Fig. 1.1)

\[
S(E) = -k_B \ln \frac{N}{M} \ln M - (N - M) \ln \left( \frac{N - M}{N} \right)
\]

where \( f_\uparrow = \frac{M}{N} \) (or \( f_\downarrow = 1 - \frac{M}{N} \)) is the probability for a spin to be up (or down). Since \( E = M\epsilon - (N - M)\frac{\epsilon}{2} \), we have \( f_\uparrow = \frac{1}{2} + \frac{E}{E_0} \) and \( f_\downarrow = \frac{1}{2} - \frac{E}{E_0} \) where \( E_0 = N\epsilon_0 \). Thus

\[
k_B^{-1} S(E) = N \left[ -\left( \frac{1}{2} + \frac{E}{E_0} \right) \ln \left( \frac{1}{2} + \frac{E}{E_0} \right) - \left( \frac{1}{2} - \frac{E}{E_0} \right) \ln \left( \frac{1}{2} - \frac{E}{E_0} \right) \right]
\]

Clearly, from the definition, the physical meaning of the entropy is

\[
\text{number of states with energy } E = e^{S(E)/k_B}
\]

1.2.2 Concept of temperature

To introduce the concept of temperature, let us put two systems of spins together. The system-1 has \( N_1 \) spins and the system-2 has \( N_2 \) spins. Let \( \tilde{E}_1, \tilde{E}_2 \) be the energies of the two systems at the beginning. The total energy is \( E = \tilde{E}_1 + \tilde{E}_2 \). If we allow the two systems to exchange their energy, then the spins in the two systems may flip up and down, and sample all the possible states with total energy \( E \). Now we like to ask what is the probability for the system-1 to have a new energy \( E_1 \)? Certainly, the system-2 will have an energy \( E_2 = E - E_1 \) when the system-1 to have a new energy \( E_1 \).

The number states with system-1 having an energy \( E_1 \) and the system-2 having an energy \( E_2 = E - E_1 \) is given by \( \Gamma_{\text{tot}} = \Gamma_1(E_1)\Gamma_2(E_2) \), or in terms of entropies:

\[
\Gamma_{\text{tot}}(E_1) = e^{k_B^{-1}S_1(E_1)} e^{k_B^{-1}S_2(E-E_1)} = e^{k_B^{-1}[S_1(E_1) + S_2(E-E_1)]}
\]

Since every possible states are equally possible, the probability for the system-1 to have an energy \( E_1 \)

\[
P(E_1) \propto e^{k_B^{-1}[S_1(E_1) + S_2(E-E_1)]}
\]

From Fig. 1.2, we see that when \( N \to \infty \), \( P(E_1) \) is almost a \( \delta \)-function. We can almost say for sure that the energy of the system-1 has such a value \( \tilde{E}_1 \) that it maximizes the total entropy \( S_1(E_1) + S_2(E-E_1) \), or

\[
S_1'(\tilde{E}_1) = S_2'(E - \tilde{E}_1)
\]
Figure 1.2: For a system of $N_1$ spins and a system of $N_2$ spins with total energy $E$, we plot the probability $P(E_1)$ for the $N_1$-spin system to have an energy $E_1$. Here $N_2 = 2N_1$ and $N_1 = 10, 100, 1000, 10000$. The total energy $E$ is chosen to be $-N_1\epsilon_0$. $P(E_1)$ reach its maximum when $E_1 = -E/3$.

Figure 1.3: The relation between temperate $T$, the inverse temperature $\beta$ with the average energy per spin $\epsilon$.

If $E_1$ at the beginning is not equal to $\bar{E}_1$, then after we bring the two spin systems together, $E_1$ will shift from $\bar{E}_1$ to $\bar{E}_1$. We see that Eq. (1.2.9) is a condition for equilibrium. It is also the maximum entropy condition. We have derived the second law of thermodynamics: as an isolated system approach to the equilibrium state, its entropy always increase (if we define the entropy as in Eq. (1.2.1)).

If we define the temperature as

$$\frac{1}{T} = \beta k_B = \frac{\partial S(E)}{\partial E}$$  \hspace{1cm} (1.2.10)

then the equilibrium condition Eq. (1.2.9) becomes

$$T_1 = T_2$$  \hspace{1cm} (1.2.11)

For our spin system

$$\frac{1}{T} = \beta k_B = k_B \frac{1}{\epsilon_0} \ln \left( \frac{\frac{1}{2}E_0 - E}{\frac{1}{2}E_0 + E} \right) = k_B \frac{1}{\epsilon_0} \ln \left( \frac{f_{\downarrow}}{f_{\uparrow}} \right)$$  \hspace{1cm} (1.2.12)

(see Fig. 1.3).
1.2.3 Curie’s law

Eq. 1.2.12 relates the temperature $T$ with the probability distribution of the spins: $f_\uparrow$ and $f_\downarrow$. We find

$$\frac{f_\uparrow}{f_\downarrow} = e^{-\epsilon_0/k_BT} \quad (1.2.13)$$

which implies that

$$f_\uparrow = \frac{e^{-\epsilon_0/k_BT}}{e^{-\epsilon_0/k_BT} + 1}, \quad f_\downarrow = \frac{1}{e^{-\epsilon_0/k_BT} + 1}.$$ 

Note that Eq. 1.2.13 is nothing but the Boltzmann distribution. So from the equal probability principle and the definition of temperature Eq. 1.2.10, we can derive the Boltzmann distribution.

For a spin-$1/2$ system in magnetic field $B$, $\epsilon_0 = g\mu_B B$. The total magnetic moment is $M = N(f_\uparrow - f_\downarrow)\frac{g\mu_B}{2}$. We find

$$M = \frac{Ng\mu_B}{2} \left( \frac{e^{-\epsilon_0/k_BT}}{e^{-\epsilon_0/k_BT} + 1} - \frac{1}{e^{-\epsilon_0/k_BT} + 1} \right)$$

$$= \frac{Ng\mu_B}{2} \tanh \frac{\epsilon_0}{2kB_T}$$

$$= \frac{Ng\mu_B}{2} \tanh \frac{g\mu_B B}{2kB_T}$$

For $B \ll \frac{k_BT}{g\mu_B}$, we have

$$M = \frac{g^2\mu_B^2N}{4kB_T} B$$

We find magnetic susceptibility $\chi = \frac{g^2\mu_B^2N}{4kB_T} \propto 1/T$. This is the Curie’s law (see Fig. 1.4).

1.2.4 Properties of entropy

Entropy is an extensive quantity

From

$$k_B^{-1}S(E) = N \left[ -\left( \frac{1}{2} + \frac{\epsilon}{\epsilon_0} \right) \ln(\frac{1}{2} + \frac{\epsilon}{\epsilon_0}) - \left( \frac{1}{2} - \frac{\epsilon}{\epsilon_0} \right) \ln(\frac{1}{2} - \frac{\epsilon}{\epsilon_0}) \right] \quad (1.2.14)$$

where $\epsilon = E/N$ is the average energy per spin, we see that entropy is proportional to $N$, the size of system. Thus $S$ is an extensive quantity. In contrast, $\epsilon$, as the average energy per spin, is an intensive quantity. The total energy $E$ is an extensive quantity and the temperature $T$ is an intensive quantity.
Entropy and energy window

From the definition of entropy

\[ S(E, \Delta E) = k_B \ln(\text{number of states with energy between } E \text{ and } E + \Delta E) \]  (1.2.15)

we see that entropy also depend on the energy window \( \Delta E \). However, in the thermodynamical limit \( N \to \infty \), such a dependence can be dropped and we can regard \( S \) as a function of \( E \) only.

To see this, we consider

\[
S(E, \alpha \Delta E) = k_B \ln(\text{number of states with energy between } E \text{ and } E + \alpha \Delta E) \\
= k_B \ln(\alpha \times (\text{number of states with energy between } E \text{ and } E + \Delta E)) \\
= S(E, \Delta E) + k_B \ln \alpha
\]  (1.2.16)

Since \( S(E, \Delta E) \sim N \), as long as \( \alpha = O(N^n), k_B \ln \alpha \) term can be dropped.

Additive property of entropy

Consider two systems both with \( N \) spins. The first system has total energy \( E_1 \) and the second \( E_2 \). The first system has \( \Gamma_1 = \Gamma(E_1) \) possible states and the second \( \Gamma_2 = \Gamma(E_2) \) possible states.

If we put the two systems together, but forbid any exchange of energy between them (see Fig. 1.5a), then the combined system will has \( \Gamma = \Gamma_1 \Gamma_2 \) possible states. The entropy of the combined system \( S = k_B \ln \Gamma \) is the sum of the sub systems

\[ S = S_1 + S_2 \]  (1.2.17)

If we allow the two system to exchange energy, the two systems will reach an equilibrium state. The subsystem will have the same average energy \( \bar{E} = (E_1 + E_2)/2 \) in the equilibrium state. The equilibrium state of the combined system will have a total energy \( 2\bar{E} \). The number of possible states become
\[ \dot{\Gamma} = \sum_{E_1} \Gamma(E_1)\Gamma(2\bar{E} - E_1), \]

it is clear that the \( \dot{\Gamma} > \Gamma = \Gamma(E_1)\Gamma(E_2) \) and the equilibrium state has a higher entropy (see Fig. 1.6). Thus reaching equilibrium always increase entropy (the second law of thermodynamics).

After the two systems reach the equilibrium, we now forbid the energy exchange. The total number states is then reduced to \( \Gamma' = \Gamma(E)\Gamma(\bar{E}) \). We like to show that \( \ln \Gamma(E)\Gamma(\bar{E}) = \ln \dot{\Gamma} \) in the thermodynamical limit, ie the system Fig. 1.5b and the system Fig. 1.5c have the same entropy. As the maximum of the \( \Gamma(E_1)\Gamma_2(2\bar{E} - E_1) \), we find \( \dot{\Gamma}' > \dot{\Gamma}/2N \), where \( 2N \) is the number of possible distinct values of \( E_1 \). We also have \( \dot{\Gamma}' < \dot{\Gamma} \). Thus

\[ \ln \dot{\Gamma} > \ln \dot{\Gamma}' > \ln(\dot{\Gamma}/2N) \quad (1.2.18) \]

or

\[ \bar{S} > \bar{S}' > \bar{S} - k_B\ln(2N) \quad (1.2.19) \]

Since \( S \) and \( S' \) is of order \( N \). In large \( N \) limit, we can regard \( \bar{S} = \bar{S}' \).

From Fig. 1.6 we also see that as the system goes from Fig. 1.5a to the equilibrium state Fig. 1.5b or Fig. 1.5c, the entropy of the system is maximized. Or equilibrium state has maximum entropy.

### Entropy and probability distribution

The entropy can be related to probability distribution. To see such a relation, let us interpret the definition of the entropy as follows: if the \( \Gamma \) states at energy \( E \) all have the same probability to appear, then the entropy is \( S = k_B\ln \Gamma \). Now the question is that if the \( \Gamma \) states have unequal probabilities to appear, then what is the entropy of the system?

From the entropy of the system of \( N \) spin-1/2 \( S = k_BN(-f_\uparrow\ln f_\uparrow - f_\downarrow\ln f_\downarrow) \) and the additive property of the entropy, we may interpret \( k_B(-f_\uparrow\ln f_\uparrow - f_\downarrow\ln f_\downarrow) \) as the entropy of a single spin-1/2. Since \( f_\uparrow \) and \( f_\downarrow \) are the probabilities for spin in the up and the down states, we see how entropy and the probabilities are related.

In general, if \( f_i \) is the probability for the \( i^{\text{th}} \) state to appear, then the entropy is

\[ S = -k_B\sum_{i=1}^{\Gamma} f_i\ln f_i, \quad (1.2.20) \]

where \( \Gamma \) is the total number of states. If all states have the same probability to appear, we have \( f_i = 1/\Gamma \) and

\[ S = -k_B\sum_{i=1}^{\Gamma} f_i\ln f_i = -k_B\sum_{i=1}^{\Gamma} \Gamma^{-1}\ln \Gamma^{-1} = k_B\ln \Gamma. \quad (1.2.21) \]

We recover the old result.

### Reversible and irreversible processes

The system in Fig. 1.5b is evolved from the system in Fig. 1.5a. There are only \( \Gamma(E_1)\Gamma(E_2) \) possible initial states. Thus there will be only \( \Gamma(E_1)\Gamma(E_2) \) possible final states. The system in Fig. 1.5b has \( \dot{\Gamma} \) states with energy \( 2\bar{E} \). But among \( \dot{\Gamma} \) possible state, only \( \Gamma(E_1)\Gamma(E_2) \) of them are the final states evolved from the system in Fig. 1.5a. But we have no clue about which are the \( \Gamma(E_1)\Gamma(E_2) \) possible final states. We lost the information. We only know the total energy of the system, and we only know the state can be in one of the \( \Gamma \) states. This is how the entropy get increased.
1.3 Application to classical ideal gas

How to count states:
Each state is described by a point in phase space \((q,p)\).
A particle has three degrees of freedom and its state is described by \((x,p_x,y,p_y,z,p_z)\).

Consider a \(N\)-particle system. How many states with total energy below \(E\). The answer is infinity. We need quantum physics to get a sensible result. Each state in a degree freedom occupies a finite area \(\Delta q \Delta p = \hbar\). For the \(N\) particle system, the phase space is \(6N\) dimensional. Each \(\hbar^{3N}\) volume in the \(6N\) dimensional phase space correspond to one state. Thus the number of states with total energy below \(E\) is given by

\[
N_<(E) = \frac{1}{\hbar^{3N}} \int \sum p_i^2/2m < E d^{3N}q d^{3N}p = V^N \frac{S_{3N}(\sqrt{2mE})^{3N}/3N}{\hbar^{3N}}
\]

where \(S_n\) is the solid angle in \(n\) dimension and \(\int_0^R S_n r^{n-1} dr = S_n R^n / n\) is the volume of a \(n\)-dimensional ball of radius \(R\). The number states between \(E\) and \(E + \Delta E\) is

\[
\Gamma(E) = N_<(E + \Delta E) - N_<(E) = \frac{V^N S_{3N}(\sqrt{2mE})^{3N-2} \sqrt{m}}{\hbar^{3N}} \Delta E
\]  

(1.3.1)
To obtain $S_n$, we note
\[
\int d^n x e^{-x^2} = \int S_n r^{n-1} dr e^{-r^2} = \frac{1}{2} S_n \int (r^2)^{(n-2)/2} dr e^{-r^2} = \frac{1}{2} S_n \Gamma(n/2) = \pi^{n/2}
\]
(1.3.2)

We find that
\[
S_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}
\]
(1.3.3)

The entropy can now be calculated as
\[
k_B^{-1} S(E) = N \ln N + N \ln v + \frac{3N}{2} \ln N + 3N \ln((2me)^{1/2}/h) + 3N \ln \sqrt{\pi} - \frac{3N}{2} \ln(3N/2) + 3N/2 + \ln \Delta E
\]
\[
= N \ln N + N \ln v + 3N \ln \left(\frac{2mE}{\hbar^2}\right) + N \left(\frac{3}{2} \ln \frac{2\pi}{3} + \frac{3}{2}\right) + \ln \Delta E
\]
(1.3.4)

where $v = V/N$ is the volume per particle and $\epsilon = E/N$ is the average energy per particle.

A big problem, the entropy is NOT extensive due to the $N \ln N$ term. We need to use a concept from quantum physics - identical particle. For identical particles
\[
N_{\leq}(E) = \frac{1}{h^{3N}N^!} \int \sum p_i^{3/2} d^{3N} p \quad (1.3.5)
\]

Using $\ln N! = N \ln N - N$, we find
\[
k_B^{-1} S(E) = N \ln \left(\frac{2mE}{\hbar^2}\right) + N \left(\frac{3}{2} \ln \frac{2\pi}{3} + \frac{5}{2}\right)
\]
(1.3.6)

For identical particles, the entropy is extensive. The entropy per particle, $s$, is given by
\[
k_B^{-1} s = k_B^{-1} S/N = \ln \left(\frac{2mE}{\hbar^2}\right) + \left(\frac{3}{2} \ln \frac{2\pi}{3} + \frac{5}{2}\right)
\]
\[
\approx \ln \left(\frac{2mE}{\hbar^2}\right)
\]
\[
= \ln \left(\frac{v}{\lambda^3}\right)
\]
(1.3.7)

Meaning: $\epsilon$ average energy per particle. $(2me)^{1/2}$ the corresponding momentum. $\lambda = h/(2me)^{1/2}$ the corresponding wave length. $v/\lambda^3$ number of wave packets that can be fitted into the volume per particle.

Classical gas: $v/\lambda^3 \gg 1$.

Quantum gas: $v/\lambda^3 \sim 1$.

(Question: is air at room temperature a quantum gas or a classical gas?)

**Thermodynamical function $E(S,V,N$)**

From $\epsilon = \frac{k^2}{2m \epsilon^2} e^{2s/3k_B}$ we get
\[
E(S,V,N) = N \frac{k^2 N^{2/3}}{2m V^{2/3}} e^{2s/3k_B}
\]
(1.3.8)
The equation of state: The temperature

\[ T = \frac{\partial E}{\partial S} = \frac{2}{3Nk_B} N \frac{h^2 N^{2/3}}{2m V^{2/3}} e^{2S/3Nk_B} \]  

(1.3.9)

The pressure

\[ P = -\frac{\partial E}{\partial V} = \frac{2}{3V} N \frac{h^2 N^{2/3}}{2m V^{2/3}} e^{2S/3Nk_B} \]  

(1.3.10)

We obtain the equation of state

\[ PV = Nk_B T \]  

(1.3.11)