

Chapter 1

Statistical Ensembles

1.1 Principle of statistical physics and ensembles

Key points:

- *All possible states appear with an equal probability.*

Statistical systems are complex systems. We do not know all the information that is needed to completely characterize the systems. For example, the liter of gas may contain 10^{22} atoms. To completely characterize such a system we need to know the three components of the velocity for each atom and the three components of the position for each atom. It is impossible to obtain 6×10^{22} real numbers to completely characterize the gas.

However, not knowing all the information needed to characterize gas does not prevent us from developing 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 detail of each atom. Not knowing every thing about the atoms does not prevent us from calculating those properties. This is the kind of problems facing statistical physics. In statistical physics we try to understand the properties of a complex system without knowing all the information of the systems. This is possible since the properties we are interested in do not depend on the details of the system.

In statistical physics there is only one principle: All possible states appear with an *equal* probability. Let us explain what we mean by the above statement. Suppose we know certain properties of a complex system. But those properties do not characterize the system completely. That means the system has a number of states that all have the same properties. Thus even after knowing those properties, we still do not know, among those possible states, which state the system is in. According to the principle of statistical physics, we say all the possible states are equally likely.

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 have the same properties. But each copy may be in a different possible state. Then “equally likely” means that each possible state appears the same number of times among the copies of the system. The copies of the system are called ensemble. We have to have an ensemble to even define the probabilities. Under the first interpretation, statistical physics is a science that deals with ensembles, rather than individual systems.

The second point of view only applies to the situation where the properties of the system are 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 second point of view may be equivalent to the first point of view. The two points of view are equivalent only when the system can visit all the possible states, many times, during the long period of time. This is the ergodic hypothesis. Not all systems are ergodic. In this class, we will take the first point of view. We regard the statistical physics as a theory for ensembles. We will apply the theory for ensembles to individual systems, assuming the systems are ergodic.

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 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

A simple example: N spins in magnetic field. Energy: $E_{\uparrow} = \epsilon_0/2$ and $E_{\downarrow} = -\epsilon_0/2$.

How many states with energy E (ie with energy between $E - \epsilon_0$ and E)? How many states with $M = \frac{E}{\epsilon_0} + \frac{N}{2}$ up-spins and $N - M$ down-spins? There are total of 2^N states

$$\begin{aligned} (1 + 1)^N &= 1^0 1^N + N 1^1 1^{N-1} + \dots + C_N^M 1^M 1^{N-M} + \dots \\ (\uparrow + \downarrow)^N &= \uparrow^0 \downarrow^N + N \uparrow^1 \downarrow^{N-1} + \dots + C_N^M \uparrow^M \downarrow^{N-M} + \dots \end{aligned} \tag{1.2.1}$$

where

$$C_N^M = \frac{N!}{M!(N-M)!} \tag{1.2.2}$$

C_N^M is the number of ways to pick M objects from N objects. We find

$$\text{number of states with } M \uparrow \text{ spins} = C_N^M \tag{1.2.3}$$

The entropy is a function of energy E which is defined as

$$S(E) = k_B \ln(\text{number of states}) = k_B \ln C_N^{E/\epsilon_0} \tag{1.2.4}$$

When n is large

$$\ln(n!) = (n + \frac{1}{2}) \ln(n + 1) - (n + 1) + \frac{1}{2} \ln(2\pi) + \dots \tag{1.2.5}$$

Thus (see Fig. 1.1)

$$\begin{aligned} k_B^{-1} S(E) &= \ln C_N^M \\ &\approx N \ln N - M \ln M - (N - M) \ln(N - M) \\ &= -M \ln\left(\frac{M}{N}\right) - (N - M) \ln\left(\frac{N - M}{N}\right) \\ &= N(-f_{\uparrow} \ln f_{\uparrow} - f_{\downarrow} \ln f_{\downarrow}) \end{aligned} \tag{1.2.6}$$

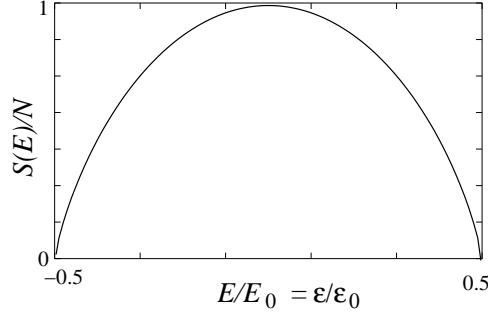


Figure 1.1: The entropy per spin, $S(E)/N$, as a function of E or ϵ the average energy per spin. The maximum entropy of a spin-1/2 spin is $k_B \ln(2) = 0.69314718056k_B$.

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

$$k_B^{-1}S(E) = N \left[-\left(\frac{1}{2} + \frac{E}{E_0}\right) \ln\left(\frac{1}{2} + \frac{E}{E_0}\right) - \left(\frac{1}{2} - \frac{E}{E_0}\right) \ln\left(\frac{1}{2} - \frac{E}{E_0}\right) \right] \quad (1.2.7)$$

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

$$\text{number of states with energy } E = e^{S(E)/k_B} \quad (1.2.8)$$

1.2.2 Concept of temperature

To introduce the concept of temperature, let us put two systems of spins together. System 1 has N_1 spins and System 2 has N_2 spins. Let $\tilde{E}_{1,2}$ 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 wondering around and sample all the possible states with total energy E . The question is what is the probability for system 1 to have an energy E_1

The number states with system 1 having an energy E_1 is

$$N(E_1) = e^{k_B^{-1}S_1(E_1)} e^{k_B^{-1}S_2(E-E_1)} = e^{k_B^{-1}[S_1(E_1)+S_2(E-E_1)]} \quad (1.2.9)$$

Every possible states are equally possible. Probability for system 1 to have an energy E_1

$$P(E_1) \propto e^{k_B^{-1}[S_1(E_1)+S_2(E-E_1)]} \quad (1.2.10)$$

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

$$S'_1(\bar{E}_1) = S'_2(E - \bar{E}_1) \quad (1.2.11)$$

If \tilde{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 \tilde{E}_1 to \bar{E}_1 . We see that Eq. (1.2.11) is a condition for equilibrium. It is also 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. (1.2.4)).

If we define the temperature as

$$\frac{1}{T} = \beta k_B = \frac{\partial S(E)}{\partial E} \quad (1.2.12)$$

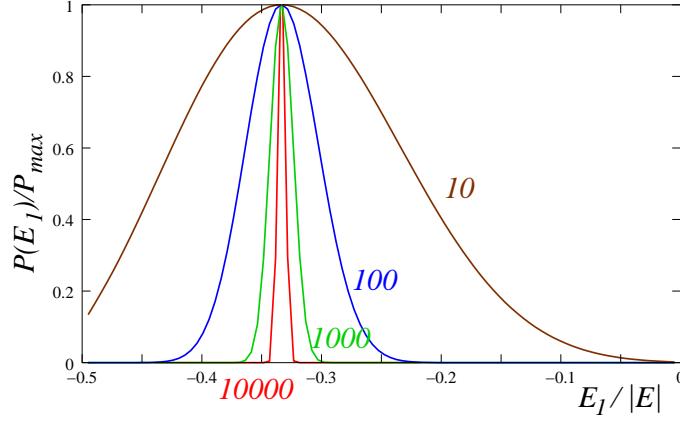


Figure 1.2: For a system of N_1 spins and a system of N_2 spins with total energy E , we plot the probability $P(E_1)$ for the N_1 -spin system to have an energy E_1 . Here $N_2 = 2N_1$ and $N_1 = 10, 100, 1000, 10000$. E is chosen to be $-N_1\epsilon_0$. $P(E_1)$ reach its maximum when $E_1 = E/3$.

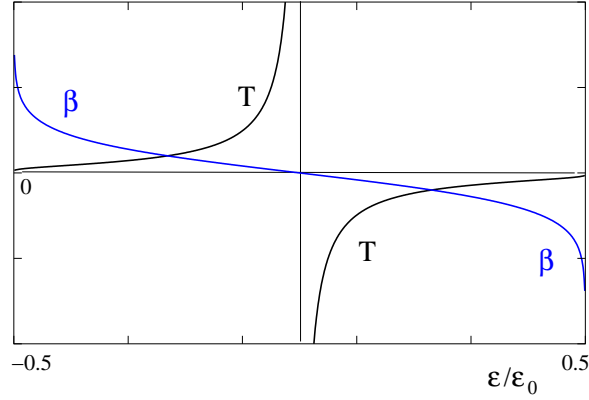


Figure 1.3: The relation between temperature T , the inverse temperature β with the average energy per spin ϵ .

then the equilibrium condition Eq. (1.2.11) becomes

$$T_1 = T_2 \quad (1.2.13)$$

For our spin system

$$\frac{1}{T} = \beta k_B = k_B \frac{1}{\epsilon_0} \ln \left(\frac{\frac{1}{2}\epsilon_0 + \epsilon}{\frac{1}{2}\epsilon_0 - \epsilon} \right) \quad (1.2.14)$$

where $\epsilon = E/N$ is the average energy per spin.

1.2.3 Curie's law

For a spin-1/2 system in magnetic field B , $\epsilon_0 = g\mu_B B$. The total magnetic energy is $\mathcal{M}B$ where \mathcal{M} is the magnetic moment. The energy per spin is $\epsilon = \mathcal{M}B/N$. From Eq. (1.2.14), we find a relation between the B -field induced magnetic moment \mathcal{M} and the temperature T

$$\frac{1}{T} = \frac{k_B}{g\mu_B B} \ln \left(\frac{g\mu_B N - 2\mathcal{M}}{g\mu_B N + 2\mathcal{M}} \right)$$

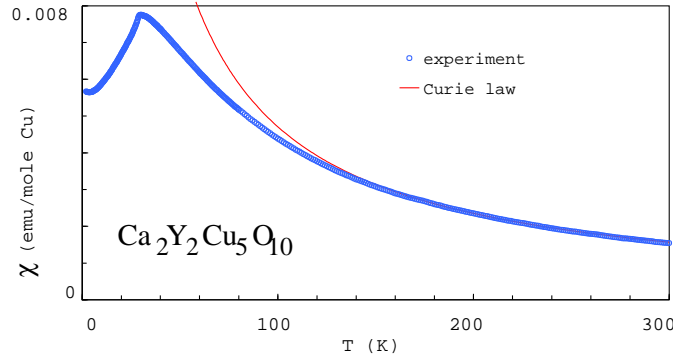


Figure 1.4: Curie's law for a magnetic material.

For $B \ll \frac{k_B T}{g\mu_B}$, we have $\mathcal{M} \ll g\mu_B N$ and

$$\mathcal{M} = \frac{g^2 \mu_B^2 N}{4k_B T} B$$

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

1.2.4 Properties of entropy

Entropy is an extensive quantity

From

$$k_B^{-1} S(E) = N \left[-\left(\frac{1}{2} + \frac{\epsilon}{\epsilon_0}\right) \ln\left(\frac{1}{2} + \frac{\epsilon}{\epsilon_0}\right) - \left(\frac{1}{2} - \frac{\epsilon}{\epsilon_0}\right) \ln\left(\frac{1}{2} - \frac{\epsilon}{\epsilon_0}\right) \right] \quad (1.2.15)$$

we see that entropy is proportional to N , the size of system. Thus S is extensive quantity. In contrast, ϵ , as the average energy per spin, is intensive quantity. The total energy E is a extensive quantity and the temperature T is an intensive quantity.

Entropy and energy window

From the definition of entropy

$$S(E, \Delta E) = k_B \ln(\text{number of states with energy between } E \text{ and } E + \Delta E) \quad (1.2.16)$$

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

To see this, we consider

$$\begin{aligned} S(E, \alpha\Delta E) &= k_B \ln(\text{number of states with energy between } E \text{ and } E + \alpha\Delta E) \\ &= k_B \ln[\alpha \times (\text{number of states with energy between } E \text{ and } E + \Delta E)] \\ &= S(E, \Delta E) + k_B \ln \alpha \end{aligned} \quad (1.2.17)$$

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

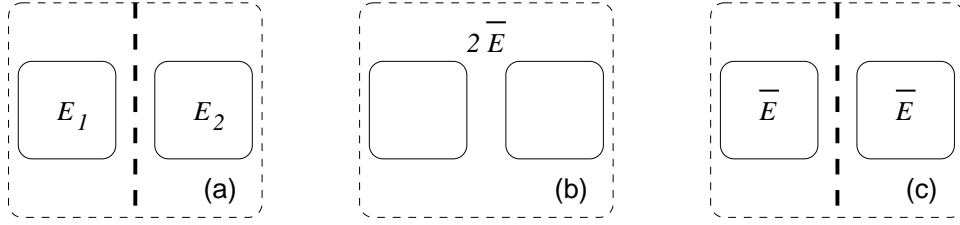


Figure 1.5: Total entropy of combined systems.

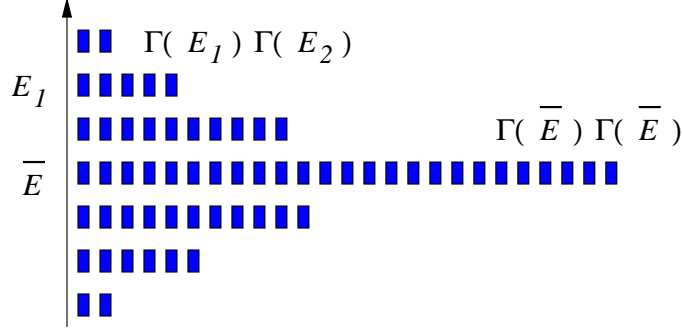


Figure 1.6: Total numbers of states in the combined system with the total energy $2\bar{E}$ and the system 1 energy E_1 .

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 $\Gamma_1 = C_N^{E_1/\epsilon_0} \equiv \Gamma(E_1)$ possible states and the second $\Gamma_2 = C_N^{E_2/\epsilon_0} = \Gamma(E_2)$ 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 have $\Gamma = \Gamma_1\Gamma_2$ possible states. The entropy of the combined system $S = k_B \ln \Gamma$ is the sum of the sub systems

$$S = S_1 + S_2 \quad (1.2.18)$$

If we allow the two systems 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 $\bar{\Gamma} = C_{2N}^{2\bar{E}/\epsilon_0}$. Since $\bar{\Gamma} = \sum_{E_1} \Gamma(E_1)\Gamma(2\bar{E} - E_1)$, it is clear that $\bar{\Gamma} > \Gamma = \Gamma(E_1)\Gamma(E_2)$ and the equilibrium state has a higher entropy (see Fig. 1.6). Thus reaching equilibrium always increases entropy (the second law of thermodynamics).

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

$$\ln \bar{\Gamma} > \ln \bar{\Gamma}' > \ln(\bar{\Gamma}/2N) \quad (1.2.19)$$

or

$$\bar{S} > \bar{S}' > \bar{S} - k_B \ln(2N) \quad (1.2.20)$$

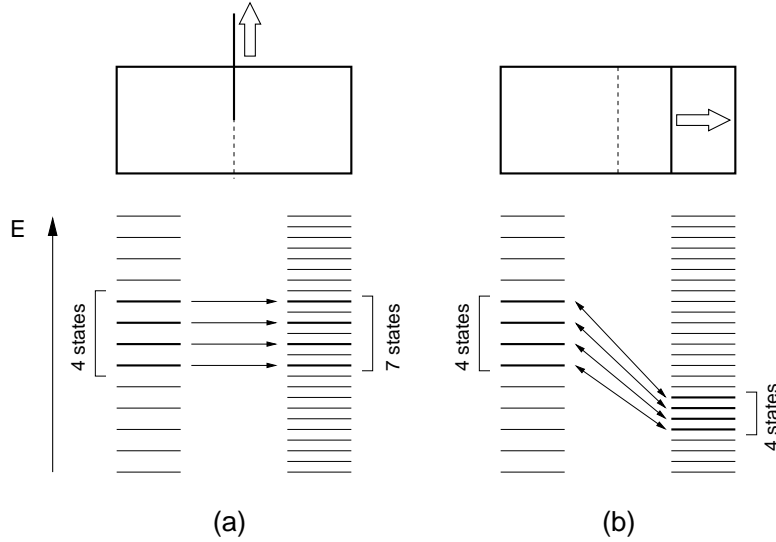


Figure 1.7: The lines represent possible states. The thick lines represent states that actually appear in the ensembles.

Since $S\bar{S}$ and \bar{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 system go 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.

Reversible and irreversible processes

The system in Fig. 1.5b is evolved from that in Fig. 1.5a. Thus there are only $\Gamma(E_1)\Gamma(E_2)$ possible initial states, and there will be only $\Gamma(E_1)\Gamma(E_2)$ possible final states. Those the system Fig. 1.5b has $\bar{\Gamma}$ states with energy $2\bar{E}$, it will only be in one of $\Gamma(E_1)\Gamma(E_2)$ possible final states. 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 $\bar{\Gamma}$ states. This is how the entropy get increased.

The evolution from Fig. 1.5a to Fig. 1.5b is also presented in Fig. 1.7a. The Fig. 1.7b represent a reversible (or adiabatic) evolution, say, caused by a change in ϵ_0 . We see that reversible (or adiabatic) processes do not change the entropy, since the number of possible states is not changed.

1.3 Application to classical ideal gas

Each degree of freedom 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 $\Delta q \Delta p = h$.* For the N particle system, the phase space is $6N$ dimensional. Each h^{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

$$N_{<}(E) = \frac{1}{h^{3N}} \int_{\sum \mathbf{p}_i^2/2m < E} d^{3N} \mathbf{q} d^{3N} \mathbf{p} = \frac{V^N S_{3N} (\sqrt{2mE})^{3N} / 3N}{h^{3N}} \quad (1.3.1)$$

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

$$\Gamma(E) = N_{<}(E + \Delta E) - N_{<}(E) = \frac{V^N S_{3N} (\sqrt{2mE})^{3N-2}}{2h^{3N}} \Delta E \quad (1.3.2)$$

To obtain S_n , we note

$$\begin{aligned} \int d^n \mathbf{x} e^{-\mathbf{x}^2} &= \int S_n r^{n-1} dr e^{-r^2} \\ &= \frac{1}{2} S_n \int (r^2)^{(n-2)/2} dr^2 e^{-r^2} \\ &= \frac{1}{2} S_n \Gamma(n/2) = \pi^{n/2} \end{aligned} \quad (1.3.3)$$

We find that

$$S_n = \frac{2\pi^{n/2}}{\Gamma(n/2)} \quad (1.3.4)$$

The entropy can now be calculated as

$$\begin{aligned} k_B^{-1} S(E) &= N \ln N + N \ln v + \frac{3N}{2} \ln N + 3N \ln((2m\epsilon)^{1/2}/h) + 3N \ln \sqrt{\pi} - \frac{3N}{2} \ln(3N/2) + 3N/2 + \ln \Delta E \\ &= N \ln N + N \ln \frac{v(2m\epsilon)^{3/2}}{h^3} + N \left(\frac{3}{2} \ln \frac{2\pi}{3} + \frac{3}{2} \right) + \ln \Delta E \end{aligned} \quad (1.3.5)$$

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

$$N_{<}(E) = \frac{1}{h^{3N} N!} \int_{\sum \mathbf{p}_i^2 / 2m < E} d^{3N} \mathbf{q} d^{3N} \mathbf{p} \quad (1.3.6)$$

Using $\ln N! = N \ln N - N$, we find

$$k_B^{-1} S(E) = N \ln \frac{v(2m\epsilon)^{3/2}}{h^3} + N \left(\frac{3}{2} \ln \frac{2\pi}{3} + \frac{5}{2} \right) \quad (1.3.7)$$

For identical particles, the entropy is extensive. The entropy per particle, s , is given by

$$\begin{aligned} k_B^{-1} s &= k_B^{-1} S/N = \ln \frac{v(2m\epsilon)^{3/2}}{h^3} + \left(\frac{3}{2} \ln \frac{2\pi}{3} + \frac{5}{2} \right) \\ &\approx \ln \frac{v(2m\epsilon)^{3/2}}{h^3} \\ &= \ln \frac{v}{\lambda^3} \end{aligned} \quad (1.3.8)$$

Meaning: ϵ average energy per particle. $(2m\epsilon)^{1/2}$ the corresponding momentum. $\lambda = h/(2m\epsilon)^{1/2}$ the corresponding wave length. v/λ^3 number 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 $\epsilon = \frac{h^2}{2mv^{2/3}} e^{2s/3k_B}$ we get

$$E(S, V, N) = N \frac{h^2 N^{2/3}}{2mV^{2/3}} e^{2S/3Nk_B} \quad (1.3.9)$$

The equation of state: The temperature

$$T = \left. \frac{\partial E}{\partial S} \right|_V = \frac{2}{3Nk_B} N \frac{h^2 N^{2/3}}{2mV^{2/3}} e^{2S/3Nk_B} \quad (1.3.10)$$

The pressure

$$P = - \left. \frac{\partial E}{\partial V} \right|_S = \frac{2}{3V} N \frac{h^2 N^{2/3}}{2mV^{2/3}} e^{2S/3Nk_B} \quad (1.3.11)$$

We obtain the equation of state

$$PV = Nk_B T \quad (1.3.12)$$