

Lecture Note 20S

Supplement to Chapter 20

Entropy
Introduction to Statistical Mechanics
Micro-canonical ensembles
Canonical ensembles

1. Definition of entropy in statistical mechanics

In statistical thermodynamics the entropy is defined as being proportional to the logarithm of the number of microscopic configurations that result in the observed macroscopic description of the thermodynamic system:

$$S = k_B \ln W$$

where k_B is the Boltzmann's constant and W is the number of microstates corresponding to the observed thermodynamic macrostate. This definition is considered to be the fundamental definition of entropy (as all other definitions can be mathematically derived from it, but not vice versa). In Boltzmann's 1896 Lectures on Gas Theory, he showed that this expression gives a measure of entropy for systems of atoms and molecules in the gas phase, thus providing a measure for the entropy of classical thermodynamics.

In 1877, Boltzmann visualized a probabilistic way to measure the entropy of an ensemble of ideal gas particles, in which he defined entropy to be proportional to the logarithm of the number of microstates such a gas could occupy. Henceforth, *the essential problem in statistical thermodynamics, i.e. according to Erwin Schrödinger, has been to determine the distribution of a given amount of energy E over N identical systems.*

Statistical mechanics explains entropy as the amount of uncertainty (or "mixedupness" in the phrase of Gibbs) which remains about a system, after its observable macroscopic properties have been taken into account. For a given set of macroscopic variables, like temperature and volume, the entropy measures the degree to which the probability of the system is spread out over different possible quantum states. The more states available to the system with higher probability, the greater the entropy. More specifically, entropy is a logarithmic measure of the density of states. In essence, the most general interpretation of entropy is as a measure of our uncertainty about a system. The equilibrium state of a system maximizes the entropy because we have lost all information about the initial conditions except for the conserved variables; maximizing the entropy maximizes our ignorance about the details of the system. This uncertainty is not of the everyday subjective kind, but rather the uncertainty inherent to the experimental method and interpretative model.

2. Boltzmann's principle

Microcanonical ensemble

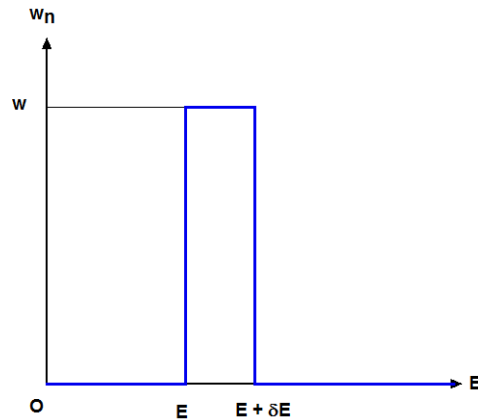
We consider a system in the energy interval between E and $E + \delta E$, where δE is the order of uncertainty. Each state in this range is assumed to have the same probability. Thus we have an ensemble characterized by the equal probability w_n of each state n , or

$$w_n = w = \text{constant for } E < E_n < E + \delta E,$$

which expresses **the principle of equal probability** as it is. The number of microscopic states accessible to a macroscopic system is called the statistical weight (thermodynamic weight). The number of states for the system with the energy between E and $E + \delta E$ (the statistical weight) may be written as

$$W(E, \delta E) = \Omega(E) \delta E$$

where $\Omega(E)$ is the density of states. This particular ensemble is known as the **microcanonical** ensemble.



Here we show that the entropy S in the equilibrium state of the system can be expressed by

$$S = k_B \ln W$$

where W is the number of states.

Suppose that the entropy S is expressed by a function W as

$$S = f(W)$$

We assume that there are two independent systems (A and B). These systems are in the macroscopic equilibrium states $|\psi_a\rangle$ and $|\psi_b\rangle$, respectively. The numbers of states for these states are given by W_a and W_b . We now consider the combined system ($C = A + B$). The number of states for the state $|\Phi_c\rangle$ ($= |\psi_a\rangle \otimes |\psi_b\rangle$) is given by

$$W_c = W_a W_b.$$

The entropy of the system C is

$$S_c = S_A + S_B$$

from the additivity of the entropy. Then we have the relation

$$f(W_a W_b) = f(W_a) + f(W_b)$$

For simplicity, we put

$$\xi = W_a, \quad \eta = W_b.$$

Then the relation is rewritten as

$$f(\xi\eta) = f(\xi) + f(\eta)$$

Taking a derivative of the both sides with respect to ξ ,

$$\eta f'(\xi\eta) = f'(\xi)$$

Taking a derivative of the both sides with respect to η ,

$$\xi f'(\xi\eta) = f'(\eta)$$

From these we get

$$\xi f'(\xi) = \eta f'(\eta) = k$$

where k is independent of ξ and η . In other words, k should be constant. The solution of the first-order differential equation is

$$f(\xi) = k \ln \xi$$

When $k = k_B$ (Boltzmann constant), the entropy is given by

$$S = k_B \ln W$$

3. Microcanonical ensemble for an ideal gas

The basic assumption of statistical mechanics is

all microstates are equally probable.

We consider the system of N free particles in a container with volume V . Each state of the system is specified by a point at $6N$ -dimensional space ($3N$ coordinates, $3N$ momenta) (so called, phase space).

$$(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) = (q_1, q_2, q_3, \dots, q_{3N}, p_1, p_2, \dots, p_{3N})$$

This state is continuous, but not discrete. For convenience, we assume that the $6N$ -dimensional phase space consists of unit cells with the volume of $(\Delta q \Delta p)^{3N}$, where the size of Δp and Δq is arbitrary. There is one state per the volume of $(\Delta q \Delta p)^{3N}$. Note that $\Delta q \Delta p = h$ (Planck's constant) from the Heisenberg's principle of uncertainty.

We define the number of states in a volume element $dq_1 dq_2 dq_3 \dots dq_{3N} dp_1 dp_2 dp_{3N}$ as

$$\frac{1}{(\Delta q \Delta p)^{3N}} dq_1 dq_2 dq_3 \dots dq_{3N} dp_1 dp_2 \dots dp_{3N}$$

The total energy E is a sum of the kinetic energy of each particle. It is independent of the $3N$ coordinates $\{\mathbf{r}_i\}$. We calculate the number of states when the total energy is between E and $E + \delta E$.

$$\begin{aligned} W(E, \delta E) &= \Omega(E) \delta E \\ &= \frac{1}{(\Delta q \Delta p)^{3N}} \int dq_1 dq_2 dq_3 \dots dq_{3N} dp_1 dp_2 \dots dp_{3N} = \frac{V^N}{(\Delta q \Delta p)^{3N}} \int dp_1 dp_2 \dots dp_{3N} \end{aligned}$$

where

$$E \leq (p_1^2 + p_2^2 + \dots + p_{3N}^2) / 2m \leq E + \delta E$$

The volume of the momentum space is the spherical shell between the sphere with radius $R = \sqrt{2m(E + \delta E)}$ and the sphere of radius $R = \sqrt{2mE}$.

We calculate the number of states between E and $E + \delta E$ as follows. First we calculate the volume of the $3N$ dimensional sphere (momentum) with radius R given by

$$R = \sqrt{2mE}$$

The volume of the sphere is obtained as

$$\frac{2}{(3N)\Gamma(3N/2)} (2\pi m E)^{3N/2}$$

where $\Gamma(x)$ is the Gamma function of x . The total number of states $N(E)$ for the system with energy between 0 and E is given by

$$N(E) = \frac{1}{(\Delta q \Delta p)^{3N}} \frac{V^N}{N!} \frac{2}{(3N)\Gamma(3N/2)} (2\pi m E)^{3N/2}$$

where $N!$ is included because N -particles are non-distinguishable. Note that $N(E)$ is introduced for the convenience of the mathematics since we consider a system having the energy only between E and $E + \delta E$. The number of states between E and $E + \delta E$ is obtained as

$$W(E, \delta E) = \Omega(E) \delta E = \frac{dN(E)}{dE} \delta E = \frac{1}{(\Delta q \Delta p)^{3N}} \frac{V^N}{N!} \frac{(2\pi m E)^{3N/2}}{\Gamma(3N/2)} \frac{\delta E}{E}$$

where $\Omega(E)$ is the density of states. We use the Heisenberg's principle of uncertainty; $\Delta q \Delta p = h$ (Planck's constant), which comes from the quantum mechanical requirement. Then we have

$$\begin{aligned} W(E, \delta E) &= \frac{dN(E)}{dE} \delta E = \frac{V^N}{N! \Gamma(3N/2)} \left(\frac{2\pi m E}{h^2} \right)^{3N/2} \frac{\delta E}{E} \\ &= \frac{V^N}{N! \Gamma(3N/2)} \left(\frac{m E}{2\pi \hbar^2} \right)^{3N/2} \frac{\delta E}{E} \end{aligned}$$

where $\hbar = h/(2\pi)$ (\hbar ; Dirac constant).

Using the Stirling's formula

$$\ln \Gamma\left(\frac{3N}{2}\right) = \frac{3N}{2} \ln\left(\frac{3N}{2}\right) - \frac{3N}{2} \quad \text{for } N \gg 1.$$

$$\ln N! = N(\ln N - 1) \quad \text{for } N \gg 1$$

Then we have

$$\begin{aligned} \ln W(E, \delta E) &= N \ln V + \frac{3N}{2} \ln\left(\frac{mE}{2\pi \hbar^2}\right) + \ln\left(\frac{\delta E}{E}\right) - N(\ln N - 1) - \left[\frac{3N}{2} \ln\left(\frac{3N}{2}\right) - \frac{3N}{2}\right] \\ &= N \left[\ln \frac{V}{N} + \frac{3}{2} \ln\left(\frac{mE}{3\pi \hbar^2 N}\right) + \frac{5}{2} \right] + \ln\left(\frac{\delta E}{E}\right) \end{aligned}$$

4. Entropy S

The entropy S is defined by

$$\begin{aligned} S &= k_B \ln W(E, \delta E) \\ &= k_B \left[\frac{5N}{2} + N \ln\left(\frac{V}{N}\right) + \frac{3N}{2} \ln\left(\frac{m}{3\pi \hbar^2} \frac{E}{N}\right) + \ln\left(\frac{\delta E}{E}\right) \right] \end{aligned}$$

In the limit of $N \rightarrow \infty$

$$S = Nk_B \left[\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{m}{3\pi\hbar^2} \frac{E}{N}\right) \right]$$

So the entropy S is found to be an extensive parameter. The entropy S depends on N , E and V :

$$S = S(N, E, V)$$

$$\begin{aligned} dS &= \frac{\partial S(N, E, V)}{\partial E} dE + \frac{\partial S(N, E, V)}{\partial V} dV \\ &= \frac{1}{T} dE + \frac{P}{T} dV \end{aligned}$$

Then we have

$$\frac{\partial S(N, E, V)}{\partial E} = k_B \frac{\partial \ln W(E, \delta E)}{\partial E} = \frac{1}{T}$$

and

$$\frac{\partial S(N, E, V)}{\partial V} = \frac{P}{T}$$

From this relation, E can be derived as a function of N , V , and T .

$$E = E(N, V, T)$$

The heat capacity C_V is given by

$$C_V = \left(\frac{\partial E}{\partial T} \right)_T$$

In the above example, we have

$$\frac{\partial S(N, E, V)}{\partial E} = \frac{1}{T} = \frac{3}{2} Nk_B \frac{1}{E}$$

or

$$E = \frac{3}{2} Nk_B T \quad (\text{internal energy})$$

and

$$\frac{\partial S(N, E, V)}{\partial V} = \frac{P}{T} = Nk_B \frac{1}{V}$$

we have

$$PV = Nk_B T \quad (\text{Boyle's law})$$

5. Typical Examples

5.1 Adiabatic free expansion (sudden expansion into a vacuum)

The free expansion is an irreversible process. Nevertheless, we can define the entropy in the reversible process (the final state and initial states are the same), given by

$$\begin{aligned} S &= Nk_B \left[\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{m}{3\pi\hbar^2} \frac{E}{N}\right) \right] \\ &= Nk_B \left[\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{m}{3\pi\hbar^2} \frac{3}{2} k_B T\right) \right] \\ &= Nk_B \left[\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{mk_B T}{2\pi\hbar^2}\right) \right] \\ &= Nk_B \left(\ln V + \frac{3}{2} \ln T \right) + \text{const} \end{aligned}$$

since $E = \frac{3}{2} Nk_B T$. This expression is exactly the same as that derived previously (Chapter 20). When the volume changes from $V = V_1$ to V_2 at constant T , the change in entropy (ΔS) is obtained as

$$\Delta S = Nk_B \ln\left(\frac{V_2}{V_1}\right)$$

5.2 Isentropic process

The entropy remains constant if

$$\ln(VT^{3/2}) = \text{const}.$$

In an expansion at constant entropy from V_1 to V_2 , we have

$$V_1 T_1^{3/2} = V_2 T_2^{3/2}$$

for an ideal monatomic gas. Since

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

we have

$$V_1 (P_1 V_1)^{3/2} = V_2 (P_2 V_2)^{3/2} \quad \text{or} \quad P_1 V_1^{5/3} = P_2 V_2^{5/3}$$

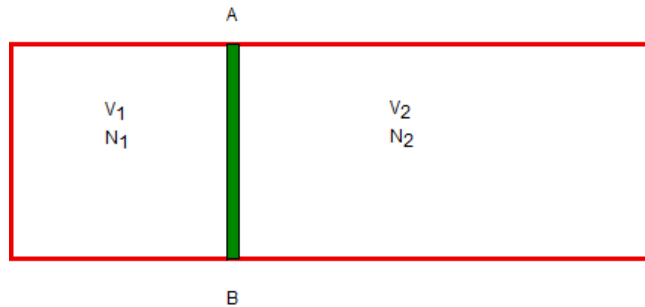
5.3 Mixing entropy of ideal gas

We consider two kinds of identical ideal gases which are separated by a barrier AB. The temperature T and the pressure P are the same.

$$\begin{aligned} P V_1 &= N_1 k_B T \\ P V_2 &= N_2 k_B T \end{aligned} \quad \text{or} \quad \frac{V_1}{N_1} = \frac{V_2}{N_2} = \frac{k_B T}{P}$$

or

$$P(V_1 + V_2) = (N_1 + N_2) k_B T \quad \frac{V_1 + V_2}{N_1 + N_2} = \frac{k_B T}{P}$$



Suppose that the barrier is open suddenly. We discuss what is the change of entropy of this system, using the expression of the entropy

$$S = N k_B \left[\frac{5}{2} + \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right]$$

Before opening the barrier AB, we have

$$S_i = S_1 + S_2$$

where

$$\begin{aligned} S_1 &= N_1 k_B \left[\frac{5}{2} + \ln\left(\frac{V_1}{N_1}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right] \\ &= N_1 k_B \left[\frac{5}{2} + \ln\left(\frac{k_B T}{P}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right] \end{aligned}$$

$$\begin{aligned}
S_2 &= N_2 k_B \left[\frac{5}{2} + \ln\left(\frac{V_2}{N_2}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right] \\
&= N_2 k_B \left[\frac{5}{2} + \ln\left(\frac{k_B T}{P}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right]
\end{aligned}$$

After opening the barrier AB, the total number of atoms is $N_1 + N_2$ and the volume is $V_1 + V_2$. Then we have the final entropy,

$$\begin{aligned}
S_f &= (N_1 + N_2) k_B \left[\frac{5}{2} + \ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right] \\
&= (N_1 + N_2) k_B \left[\frac{5}{2} + \ln\left(\frac{k_B T}{P}\right) + \frac{3}{2} \ln(T) + \alpha_0 \right]
\end{aligned}$$

Since

$$\Delta S = S_f - (S_1 + S_2) = 0$$

as is expected (the reversible process), we have no change of entropy in this event.

((Gibbs paradox))

This success is partly due to the $N!$ term in the numerator of $W(\Omega, \delta E)$. This is closely related to the fact that the particles are not distinguishable in our system.

((Micro-canonical ensemble))

So far we consider the micro-canonical ensemble, where the system is isolated from its surrounding. The energy of the system is conserved. It is assumed that the system of the energy has E and $E + \delta E$, where dE is a small width. The concept of the thermal reservoir does not appear. Since the energy of the system is constant, the possible microstates have the same probability. For the energy E , the volume V , and the number of particles, one can obtain the number of the possible microstates. Then the entropy $S(E, N, V)$ can be defined by

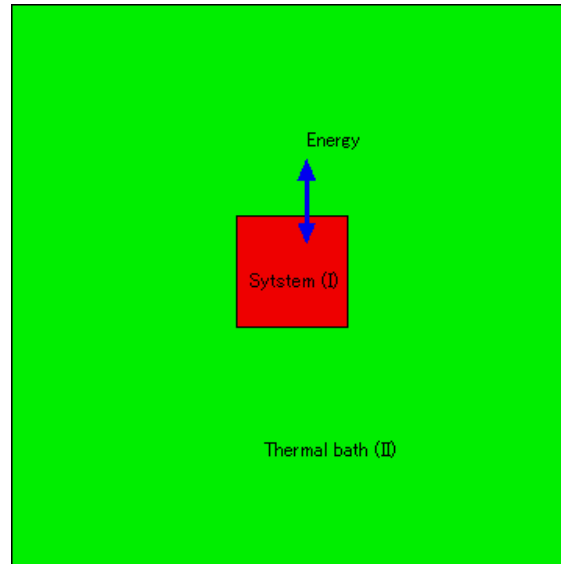
$$S = k_B \ln W(E, \delta E).$$

6. Canonical ensemble(system with constant temperature)

The theory of the micro-canonical ensemble is useful when the system depends on N , E , and V . In principle, this method is correct. In real calculations, however, it is not so easy to calculate the number of states $W(E, \delta E)$ in general case. We have an alternative method, which is much useful for the calculation in the real systems. The formulation of the canonical ensemble is a little different from that of the micro-canonical ensemble. Both of these ensembles lead to the same result for the same macro system.

Canonical ensemble: (N, T, V , constant)

Suppose that the system depends on N , T , and \mathcal{V} . A practical method of keeping the temperature of a system constant is to immerse it in a very large material with a large heat capacity. If the material is very large, its temperature is not changed even if some energy is given or taken by the system in contact. Such a heat reservoir serves as a thermostat.



We consider the case of a small system S(I) in thermal contact with a heat reservoir (II). The system S(I) is in thermal equilibrium with a reservoir W(II). S(I) and W(II) have a common temperature T . The system S(I) is a relatively small macroscopic system. The energy of S(I) is not fixed. It is only the total energy of the combined system.

$$E_T = E_{II} + E_i$$

We assume that $W_{II}(E_{II})$ is the number of states where the thermal bath has the energy E_{II} . If S(I) is in the **one definite state** $|i\rangle$, the probability of finding the system (I) in the state $|i\rangle$, is proportional to $W_{II}(E_{II})$. The thermal bath is in one of the many states with the energy $E_T - E_i$

$$p_i \propto W_{II}(E_{II}) = W_{II}(E_T - E_i)$$

or

$$\ln p_i = \ln[W_{II}(E_T - E_i)] + const$$

Since

$$E_T \gg E_i$$

$\ln[W_{II}(E_T - E_i)]$ can be expanded as

$$\ln[W_{II}(E_T - E_i)] = \ln W_{II}(E_T) - \left. \frac{d \ln W_{II}(E_{II})}{dE_{II}} \right|_{E_T} E_i$$

Then we obtain

$$p_i \propto \exp\left(-\left. \frac{d \ln W_{II}(E_{II})}{dE_{II}} \right|_{E_T} E_i\right) \quad (1)$$

Here we notice the definition of entropy and temperature for the reservoir as the micro-canonical ensemble:

$$S_{II} = k_B \ln W_{II}(E_{II})$$

and

$$\frac{\partial S_{II}}{\partial E_{II}} = \frac{1}{T_{II}}$$

or

$$\left. \frac{d \ln W_{II}(E_{II})}{dE_{II}} \right|_{E_T} = \frac{1}{k_B} \frac{\partial S_{II}}{\partial E_{II}} = \frac{1}{k_B T_{II}}$$

In thermal equilibrium, we have

$$T_{II} = T_i = T$$

Then Eq.(1) can be rewritten as

$$p_i \propto \exp\left(-\frac{E_i}{k_B T}\right) = \exp(-\beta E_i)$$

where $\beta = 1/(k_B T)$. This is called a Boltzmann factor. We define the partition function Z as

$$Z = \sum_i e^{-\beta E_i}$$

The probability is expressed by

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

The summation in Z is over all states $|i\rangle$ of the system. We note that

$$\sum_i p(E_i) = 1$$

The average energy of the system is given by

$$E = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} = -\frac{\partial \ln Z}{\partial \beta}$$

since

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{1}{Z} \sum_i (-E_i) e^{-\beta E_i} = -\frac{1}{Z} \sum_i E_i e^{-\beta E_i}$$

Note that

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{\frac{\partial \beta}{\partial T}} \frac{\partial \ln Z}{\partial T} = -k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

In summary, the representative points of the system I are distributed with the probability density proportional to $\exp(-\beta E_i)$. This is called the **canonical ensemble**, and this distribution of representative points is called the canonical distribution. The factor $\exp(-\beta E_i)$ is often referred to as the Boltzmann factor.

7. Pressure

The pressure P is defined as

$$P = \sum_i P_i \frac{1}{Z} e^{-\beta E_i} = \frac{1}{Z} \sum_i \left(-\frac{\partial E_i}{\partial V}\right) e^{-\beta E_i} = \frac{1}{Z} \frac{1}{\beta} \frac{\partial Z}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

Here we define the Helmholtz free energy F as

$$F = E - ST.$$

$$\begin{aligned} dF &= dE - SdT - TdS \\ &= TdS - PdV - SdT - TdS \\ &= -PdV - SdT \end{aligned}$$

F is a function of T and V . From this equation, we have

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

8. Helmholtz free energy and entropy

The Helmholtz free energy F is given by

$$F = -k_B T \ln Z$$

((Proof))

We note that

$$\frac{\partial}{\partial T} \left(\frac{F}{T} \right) = \frac{T \frac{\partial F}{\partial T} - F}{T^2} = \frac{-ST - F}{T^2} = -\frac{E}{T^2} = -k_B \frac{\partial}{\partial T} \ln Z,$$

which leads to

$$F = -k_B T \ln Z$$

What is the expression for the entropy in a canonical ensemble? The entropy is given by

$$S = \frac{E - F}{T}$$

where E is the average energy of the system,

$$E = -\frac{\partial \ln Z}{\partial \beta}$$

Then entropy S is rewritten as

$$\begin{aligned}
S &= -\frac{1}{T} \frac{\partial \ln Z}{\partial \beta} + k_B \ln Z \\
&= \frac{1}{T} \frac{1}{Z} \sum_i E_i e^{-\beta E_i} + k_B \ln Z \\
&= k_B \beta \sum_i E_i \frac{e^{-\beta E_i}}{Z} + k_B \ln Z \\
&= k_B \sum_i \beta E_i p_i + k_B \ln Z \\
&= k_B \sum_i (-\ln p_i - \ln Z) p_i + k_B \ln Z \\
&= -k_B \sum_i p_i \ln p_i
\end{aligned}$$

or

$$S = -k_B \sum_i p_i \ln p_i,$$

where p_i is that the probability of the $|i\rangle$ state and is given by

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

The logarithm of p_i is described by

$$\ln p_i = -\beta E_i - \ln Z$$

((Note))

We finally get a useful expression for the entropy which can be available for the information theory.

$$S = -k_B \sum_i p_i \ln p_i.$$

Suppose that there are 50 boxes. There is one jewel in one of 50 boxes. p_i is the probability of finding one jewel in the i -th box for one trial.

(a) There is no hint where the jewel is.

$$p_1 = p_2 = \dots = p_{50} = \frac{1}{50}$$

$$S = -k_B \sum_s p_s \ln p_s = -k_B \sum_{s=1}^{50} \frac{1}{50} \ln\left(\frac{1}{50}\right) = 3.91k_B$$

(b) There is a hint that the jewel is in one of the box with even number.

$$p_1 = p_3 = \dots = p_{49} = 0$$

$$p_2 = p_4 = \dots = p_{50} = \frac{1}{25}$$

$$S = -k_B \sum_s p_s \ln p_s = -k_B \sum_{s=\text{even}} \frac{1}{25} \ln\left(\frac{1}{25}\right) = 3.219k_B$$

(c) If you know that the jewel is in the 10-th box,

$$p_{10} = 1$$

$$p_s = 0 \quad (s \neq 10)$$

$$S = -k_B p_{10} \ln p_{10} = 0$$

If you know more information, the information entropy becomes smaller.

9. Application

9.1. Partition function Z

The partition function Z for the ideal gas can be calculated as

$$Z = \frac{V^N}{N! h^{3N}} \left[\int_{-\infty}^{\infty} dp \exp\left(-\frac{p^2}{2mk_B T}\right) \right]^{3N} = \frac{V^N}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{3N/2}$$

Using this expression of Z , the Helmholtz free energy F can be calculated as

$$F = Nk_B T \left[-\ln\left(\frac{V}{N}\right) - \frac{3}{2} \ln\left(\frac{2\pi mk_B T}{h^2}\right) - 1 \right].$$

The internal energy E is

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} Nk_B T.$$

The heat capacity C_V at constant volume is given by

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk_B.$$

The entropy S is

$$S = \frac{E - F}{T} = Nk_B \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{mk_B T}{2\pi\hbar^2}\right) + \frac{5}{2} \right].$$

The pressure P is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V}.$$

9.2 Maxwell's distribution function

The Maxwell distribution function can be derived as follows.

$$n(\mathbf{v})d\mathbf{v} = n(v)4\pi v^2 dv = f(v)dv = A \exp\left(-\frac{mv^2}{2k_B T}\right)4\pi v^2 dv$$

The normalization condition:

$$\int n(\mathbf{v})d\mathbf{v} = \int n(v)4\pi v^2 dv = \int f(v)dv = 1$$

The constant A is calculated as

$$A = \left(\frac{m}{2\pi k_B T}\right)^{3/2}.$$

Then we have

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right).$$

Since $M = m N_A$ and $R = N_A k_B$, we have

$$f(v) = \left(\frac{M}{2\pi RT}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{Mv^2}{2RT}\right)$$

which agrees with the expression of $f(v)$ in Chapter 19.

((Mathematica))


```
f1 = Integrate[Exp[-m v^2 / (2 kB T)] 4 π v^2, {v, 0, ∞},
GenerateConditions -> False]
```

$$\frac{2 \sqrt{2} \pi^{3/2}}{\left(\frac{m}{kB T}\right)^{3/2}}$$

```
eq1 = A f1 == 1;
```

```
Solve[eq1, A]
```

$$\left\{ \left\{ A \rightarrow \frac{\left(\frac{m}{kB T}\right)^{3/2}}{2 \sqrt{2} \pi^{3/2}} \right\} \right\}$$

10. Comparison of the expression of S in the canonical ensemble with the original definition of S in the microcanonical ensemble

The partition function Z can be written as

$$Z = \sum_i e^{-\beta E_i} = \int \Omega(\varepsilon) e^{-\beta \varepsilon} d\varepsilon$$

where we use ε instead of E (or E_j) in the expression. The partition function Z is the Laplace transform of the density of states, $\Omega(\varepsilon)$. Here we show that

$$Z = \int \Omega(\varepsilon) e^{-\beta \varepsilon} d\varepsilon = \int \psi(\varepsilon) d\varepsilon = \sqrt{2\pi\sigma^*} \Omega(\varepsilon^*) \exp(-\beta \varepsilon^*)$$

If the function $\psi(\varepsilon)$ is given by

$$\psi(\varepsilon) = \Omega(\varepsilon) e^{-\beta \varepsilon}.$$

We assume that $\psi(\varepsilon)$ can be approximated by a Gaussian function

$$\psi(\varepsilon) = \psi(\varepsilon^*) \exp\left[-\frac{(\varepsilon - \varepsilon^*)^2}{2(\sigma^*)^2}\right]$$

where

$$\psi(\varepsilon^*) = \Omega(\varepsilon^*) \exp(-\beta \varepsilon^*)$$

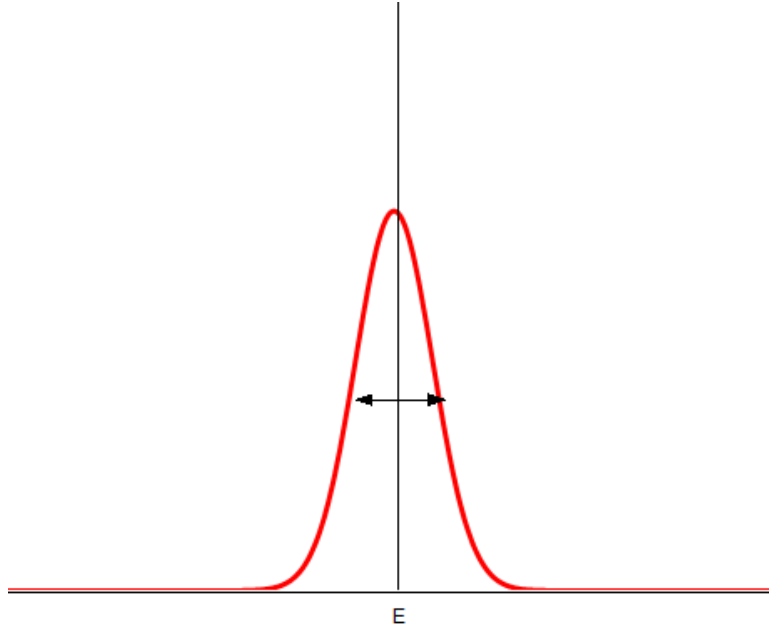


Fig. $\psi(\varepsilon)$ vs ε . $\psi(\varepsilon)$ has a Gaussian distribution with the width σ around $\varepsilon = \varepsilon^* = E$.

The function $\psi(\varepsilon)$ has a local maximum at $\varepsilon = \varepsilon^* = E$. The logarithm of $\psi(\varepsilon)$ is rewritten as

$$\begin{aligned}\ln \psi(\varepsilon) &= \ln[\Omega(\varepsilon) \exp(-\beta\varepsilon)] \\ &= \ln[\Omega(\varepsilon)] - \beta\varepsilon\end{aligned}$$

We take the derivative of $\ln \psi(\varepsilon)$ with respect to ε ,

$$\begin{aligned}\frac{\psi'(\varepsilon)}{\psi(\varepsilon)} &= \frac{\Omega'(\varepsilon)}{\Omega(\varepsilon)} - \beta \\ &= \frac{d \ln \Omega(\varepsilon)}{d\varepsilon} - \beta\end{aligned}$$

where

$$\left. \frac{d \ln \Omega(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\varepsilon^*} = \beta$$

since

$$\psi'(\varepsilon^*) = 0.$$

Here we define the number of states $\mathcal{W}(\varepsilon, \delta\varepsilon)$ by

$$W(\varepsilon, \delta\varepsilon) = \Omega(\varepsilon^*) \delta\varepsilon = \sqrt{2\pi\sigma^*} \Omega(\varepsilon^*)$$

Then we have

$$\left. \frac{d \ln W(\varepsilon, \delta\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\varepsilon^*} = \beta \quad (1)$$

since

$$\begin{aligned} \ln W(\varepsilon, \delta\varepsilon) &= \ln \Omega(\varepsilon^*) + \ln \delta\varepsilon \\ \left. \frac{\partial \ln W(\varepsilon, \delta\varepsilon)}{\partial \varepsilon} \right|_{\varepsilon=\varepsilon^*} &= \left. \frac{\partial \ln \Omega(\varepsilon)}{\partial \varepsilon} \right|_{\varepsilon=\varepsilon^*} \end{aligned}$$

with fixed $\delta\varepsilon$. We note that

$$\begin{aligned} Z &= \int \psi(\varepsilon) d\varepsilon = \psi(\varepsilon^*) \int_0^{\infty} \exp\left[-\frac{(\varepsilon - \varepsilon^*)^2}{2(\sigma^*)^2}\right] d\varepsilon = \psi(\varepsilon^*) \sqrt{2\pi\sigma^*} \\ &= \sqrt{2\pi\sigma^*} \Omega(\varepsilon^*) \exp(-\beta\varepsilon^*) \end{aligned}$$

Then we have

$$\ln Z = \ln[\sqrt{2\pi\sigma^*} \Omega(\varepsilon^*)] - \beta\varepsilon^*$$

The entropy S is calculated as

$$\begin{aligned} S &= -\frac{1}{T} \frac{\partial \ln Z}{\partial \beta} + k_B \ln Z \\ &= \frac{\varepsilon^*}{T} + k_B \ln[\sqrt{2\pi\sigma^*} \Omega(\varepsilon^*)] - \frac{\varepsilon^*}{T} \\ &= k_B \ln[\sqrt{2\pi\sigma^*} \Omega(\varepsilon^*)] \\ &= k_B \ln W(\varepsilon, \delta\varepsilon) \end{aligned} \quad (2)$$

Using Eqs.(1) and (2), we get

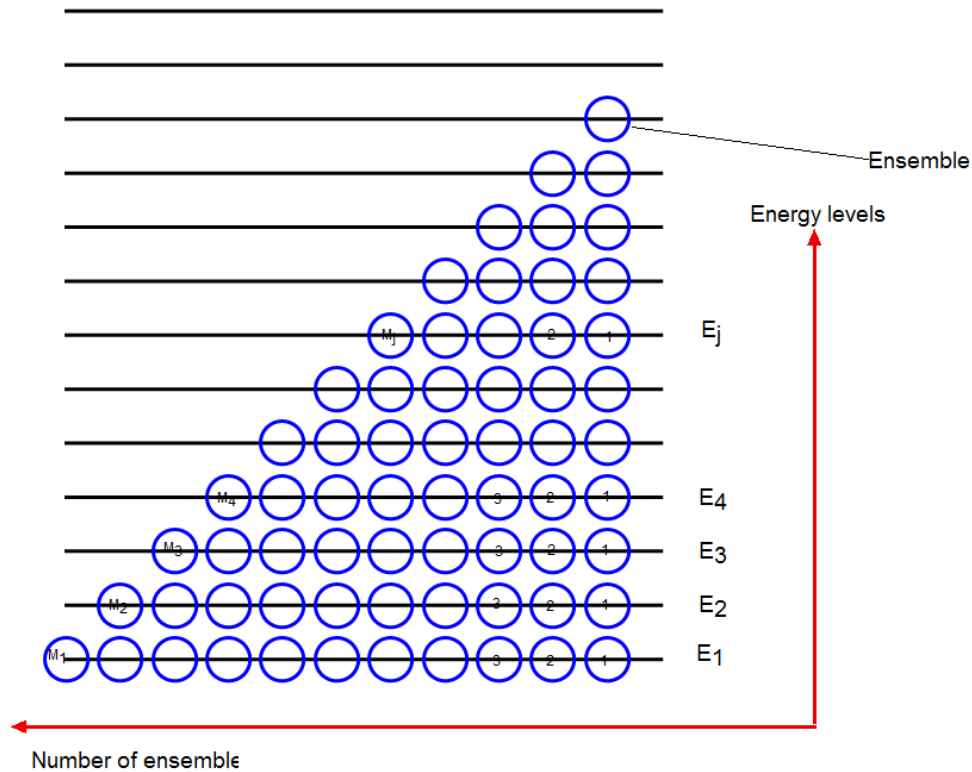
$$\frac{\partial S}{\partial E} = k_B \beta = \frac{1}{T}$$

or

$$\frac{\partial \ln W(\varepsilon, \delta\varepsilon)}{\partial \varepsilon} = \frac{1}{T}$$

11. Boltzmann-Planck's method

Finally we show the standard method of the derivation, which characterizes well the theory of canonical ensembles.



We consider the way of distributing M total ensembles among states with energies E_j . Let M_j be the number of ensembles in the energy level E_j ; M_1 ensembles for the energy E_1 , the M_2 ensembles for the energy E_2 , and so on. The number of ways of distributing M ensembles is given by

$$W = \frac{M!}{M_1! M_2! \dots}$$

where

$$\sum_j M_j = M$$

and the average energy $\langle E \rangle$ is given by

$$\langle E \rangle = \sum_j E_j \frac{M_j}{M}$$

The entropy S is proportional to $\ln W$,

$$\ln W = \ln M! - \sum_j \ln(M_j!)$$

Using the Stirling's formula

$$\begin{aligned} \ln W &= M(\ln M - 1) - \sum_j M_j(\ln M_j - 1) \\ &= M \ln M - \sum_j M_j \ln M_j \end{aligned}$$

in the limit of large M and M_j . We note that the probability of finding the state $|j\rangle$ is simply given by

$$P(E_j) = \frac{M_j}{M}$$

Then we have

$$\begin{aligned} \frac{1}{M} \ln W &= \ln M - \frac{1}{M} \sum_j M_j \ln M_j \\ &= \ln M - \frac{1}{M} \sum_j MP(E_j) \ln[MP(E_j)] \\ &= \ln M - \sum_j P(E_j) \ln[P(E_j) + \ln M] \\ &= - \sum_j P(E_j) \ln[P(E_j)] \end{aligned}$$

which is subject to the conditions

$$\begin{aligned} \sum_j P(E_j) &= 1 \\ \sum_j E_j P(E_j) &= \langle E \rangle \end{aligned}$$

Treating $P(E_j)$ as continuous variables, we have the variational equation

$$\begin{aligned} \delta \left[\sum_j P(E_j) \ln P(E_j) + \alpha P(E_j) + \beta E_j P(E_j) \right] \\ = \sum_j \{ \ln P(E_j) + (\alpha + 1) + \beta E_j \} P(E_j) = 0 \end{aligned}$$

which gives $P(E_j)$ for the maximum W . Here α and β are Lagrange's indeterminate multipliers. Thus we obtain

$$\ln P(E_j) + (\alpha + 1) + \beta E_j = 0$$

or

$$P(E_j) = C \exp[-\beta E_j]$$

or

$$P(E_j) = \frac{1}{Z(\beta)} \exp(-\beta E_j)$$

where

$$Z(\beta) = \sum_j \exp(-\beta E_j)$$

and

$$\beta = 1/k_B T.$$

With the above $P(E_j)$, the entropy S is expressed by

$$\begin{aligned} S &= k_B \ln W = \\ &= -M k_B \sum_j P(E_j) \ln[P(E_j)] \end{aligned}$$

for the total system composed of M ensembles. Therefore, the entropy of each ensemble is

$$S = -k_B \sum_j P(E_j) \ln[P(E_j)]$$

12. Density of states for quantum box (ideal gas)

(a) Energy levels in 1D system

We consider a free electron gas in 1D system. The Schrödinger equation is given by

$$H\psi_k(x) = \frac{p^2}{2m} \psi_k(x) = -\frac{\hbar^2}{2m} \frac{d^2 \psi_k(x)}{dx^2} = \varepsilon_k \psi_k(x), \quad (1)$$

where

$$p = \frac{\hbar}{i} \frac{d}{dx},$$

and ε_k is the energy of the particle in the orbital.

The orbital is defined as a solution of the wave equation for a system of only one electron: ⟨⟨one-electron problem⟩⟩.

Using a periodic boundary condition: $\psi_k(x + L) = \psi_k(x)$, we have

$$\psi_k(x) \sim e^{ikx}, \quad (2)$$

with

$$\varepsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L} n \right)^2,$$

$$e^{ikL} = 1 \text{ or } k = \frac{2\pi}{L} n,$$

where $n = 0, \pm 1, \pm 2, \dots$, and L is the size of the system.

(b) Energy levels in 3D system

We consider the Schrödinger equation of an electron confined to a cube of edge L .

$$H\psi_k = \frac{\mathbf{p}^2}{2m} \psi_k = -\frac{\hbar^2}{2m} \nabla^2 \psi_k = \varepsilon_k \psi_k. \quad (3)$$

It is convenient to introduce wavefunctions that satisfy periodic boundary conditions. Boundary condition (Born-von Karman boundary conditions).

$$\psi_{\mathbf{k}}(x + L, y, z) = \psi_{\mathbf{k}}(x, y, z),$$

$$\psi_{\mathbf{k}}(x, y + L, z) = \psi_{\mathbf{k}}(x, y, z),$$

$$\psi_{\mathbf{k}}(x, y, z + L) = \psi_{\mathbf{k}}(x, y, z).$$

The wavefunctions are of the form of a traveling plane wave.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (4)$$

with

$$k_x = (2\pi/L) n_x, (n_x = 0, \pm 1, \pm 2, \pm 3, \dots),$$

$$k_y = (2\pi/L) n_y, (n_y = 0, \pm 1, \pm 2, \pm 3, \dots),$$

$$k_z = (2\pi/L) n_z, (n_z = 0, \pm 1, \pm 2, \pm 3, \dots).$$

The components of the wavevector \mathbf{k} are the quantum numbers, along with the quantum number m_s of the spin direction. The energy eigenvalue is

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} \mathbf{k}^2. \quad (5)$$

Here

$$\mathbf{p} \psi_{\mathbf{k}}(\mathbf{r}) = \frac{\hbar}{i} \nabla_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) = \hbar \mathbf{k} \psi_{\mathbf{k}}(\mathbf{r}). \quad (6)$$

So that the plane wave function $\psi_{\mathbf{k}}(\mathbf{r})$ is an eigen-function of \mathbf{p} with the eigenvalue $\hbar \mathbf{k}$. The ground state of a system of N electrons, the occupied orbitals are represented as a point inside a sphere in \mathbf{k} -space.

(c) Density of states

Because we assume that the electrons are non-interacting, we can build up the N -electron ground state by placing electrons into the allowed one-electron levels we have just found. The one-electron levels are specified by the wave-vectors \mathbf{k} and by the projection of the electron's spin along an arbitrary axis, which can take either of the two values $\pm \hbar/2$. Therefore associated with each allowed wave vector \mathbf{k} are two levels:

$$|\mathbf{k}, \uparrow\rangle, |\mathbf{k}, \downarrow\rangle.$$

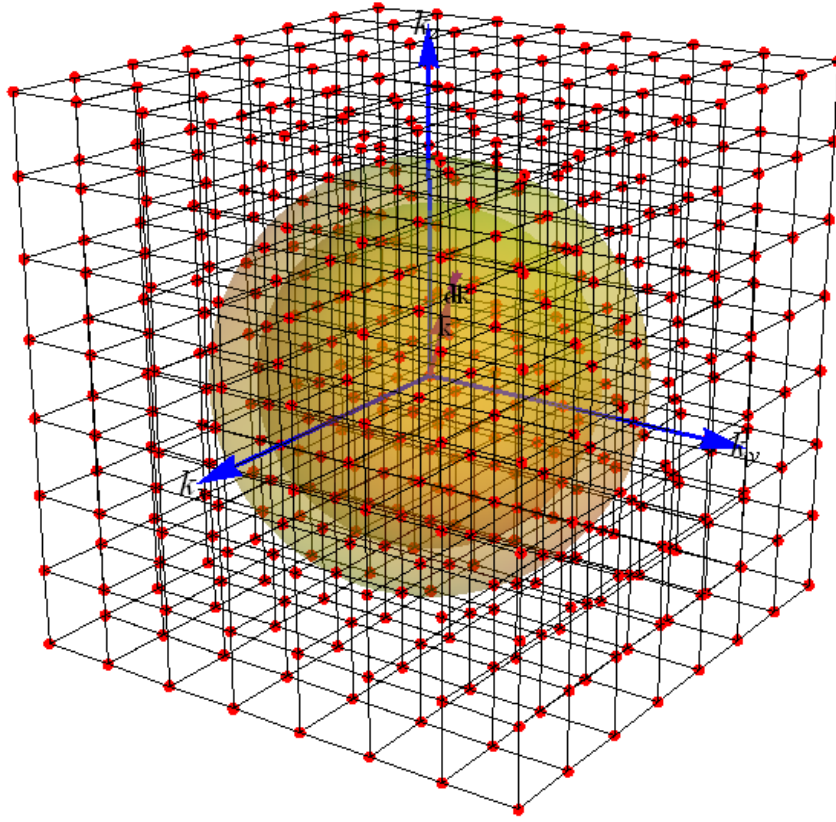


Fig. Density of states in the 3D k -space. There is one state per $(2\pi/L)^3$.

There is one state per volume of k -space $(2\pi/L)^3$. We consider the number of one-electron levels in the energy range from ε to $\varepsilon+d\varepsilon$; $D(\varepsilon)d\varepsilon$

$$\int D(\varepsilon)d\varepsilon = \frac{L^3}{(2\pi)^3} \int 4\pi k^2 dk, \quad (13)$$

where $D(\varepsilon)$ is called a density of states.

13. Application of canonical ensemble for ideal gas

(b) Partition function for the system with one atom; Z_1

The partition function Z_1 is given by

$$\begin{aligned}
Z &= \sum_{\mathbf{k}} \exp\left(-\frac{\beta \hbar^2}{2m} \mathbf{k}^2\right) \\
&= \frac{V}{(2\pi)^3} \int d\mathbf{k} \exp\left(-\frac{\beta \hbar^2}{2m} \mathbf{k}^2\right) \\
&= \frac{V}{(2\pi)^3} \int 4\pi k^2 dk \exp\left(-\frac{\beta \hbar^2}{2m} k^2\right) \\
&= \frac{V}{8\pi^2} \sqrt{\pi} C^{-3/2}
\end{aligned}$$

where $V = L^3$,

$$C = \frac{\beta \hbar^2}{2m}, \quad \beta = \frac{1}{k_B T}$$

((Mathematica))

```

Clear["Global`*"];
f1 =  $\frac{V}{(2\pi)^3} 4\pi k^2 \text{Exp}[-C1 k^2]$ ;
Integrate[f1, {k, 0,  $\infty$ }] //
Simplify[#, C1 > 0] &

 $\frac{V}{8 C1^{3/2} \pi^{3/2}}$ 

```

Then the partition function Z_1 can be rewritten as

$$Z_1 = \frac{V \sqrt{\pi}}{8\pi^2 \left(\frac{\hbar^2}{2mk_B T}\right)^{3/2}} = \frac{V}{\left(\frac{2\pi \hbar^2}{mk_B T}\right)^{3/2}} = V \left(\frac{mk_B T}{2\pi \hbar^2}\right)^{3/2} = n_Q V$$

where n_Q is a quantum concentration and is defined by

$$n_Q = \left(\frac{mk_B T}{2\pi \hbar^2}\right)^{3/2}.$$

n_Q is the concentration associated with one atom in a cube of side equal to the thermal average de Broglie wavelength.

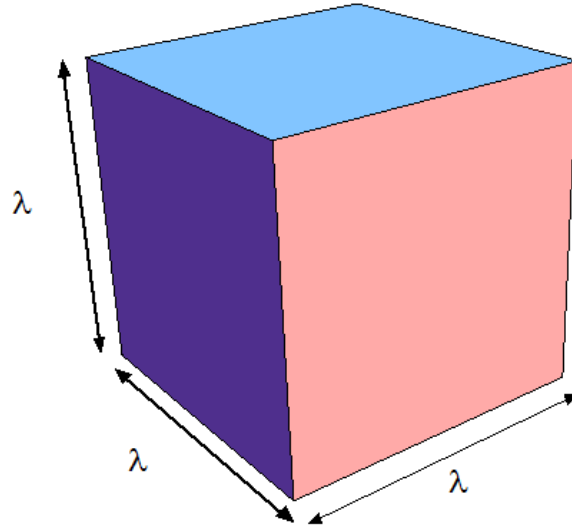


Fig. Definition of quantum concentration. The de Broglie wavelength is on the order of interatomic distance.

$$p = m\langle v \rangle = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda},$$

$$\lambda = \frac{2\pi\hbar}{m\langle v \rangle},$$

where $\langle v \rangle$ is the average thermal velocity of atoms. Using the equipartition law, we get the relation

$$\frac{1}{2} m\langle v \rangle^2 = \frac{3}{2} k_B T, \quad \text{or} \quad \langle v \rangle = \sqrt{\frac{3k_B T}{m}},$$

Then we have

$$\lambda = \frac{2\pi\hbar}{m\langle v \rangle} = \frac{2\pi\hbar}{m\sqrt{\frac{3k_B T}{m}}} = \frac{2\pi\hbar}{\sqrt{3}\sqrt{mk_B T}} = \sqrt{\frac{2\pi}{3}} \sqrt{\frac{2\pi\hbar^2}{mk_B T}} = 1.447 \frac{1}{n_Q^{1/3}} \approx \frac{1}{n_Q^{1/3}}$$

where

$$n_Q = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}$$

It follows that

$$n_Q \approx \frac{1}{\lambda^3}.$$

((Definition))

$$\frac{n}{n_Q} \ll 1 \quad \rightarrow \text{classical regime}$$

An ideal gas is defined as a gas of non-interacting atoms in the classical regime.

((Example))

⁴He gas at $P = 1$ atm and $T = 300$ K, the concentration n is evaluated as

$$n = \frac{N}{V} = \frac{P}{k_B T} = 2.446 \times 10^{19} / \text{cm}^3.$$

The quantum concentration n_Q is calculated as

$$n_Q = 7.8122 \times 10^{24} / \text{cm}^3$$

which means that $n \ll n_Q$ in the classical regime. Note that the mass of ⁴He is given by

$$m = 4u = 6.6422 \times 10^{-24} \text{ g.}$$

where u is the atomic unit mass.

((Mathematica))

```
Clear["Global`*"];
rule1 = {kB → 1.3806504 × 10-16,
  NA → 6.02214179 × 1023,
  ħ → 1.054571628 × 10-27,
  amu → 1.660538782 × 10-24,
  atm → 1.01325 × 106};
```

```
T1 = 300; P1 = 1 atm /. rule1;
```

```
m1 = 4 amu /. rule1
```

```
6.64216 × 10-24
```

```
nQ = ( (m1 kB T1) / (2 π ħ2) )3/2 /. rule1
```

```
7.81219 × 1024
```

```
n1 = P1 / (kB T1) /. rule1
```

```
2.44631 × 1019
```

(b) Partition function of the system with N atoms

Suppose that the gas contains N atoms in a volume V . The partition function Z_N , which takes into account of indistinguishability of the atoms (divided by the factor $N!$), is given by

$$Z_N = \frac{Z_1^N}{N!}.$$

Using $Z_1 = n_Q V$, we get

$$\begin{aligned} \ln Z_N &= N \ln(n_Q V) - \ln N! \\ &= N[\ln(n_Q V) + 1 - \ln N] \end{aligned}$$

where we use the Stirling's formula

$$N! \approx N \ln N - N = N(\ln N - 1),$$

in the limit of large N . The Helmholtz free energy is given by

$$\begin{aligned}
 F &= -k_B T \ln Z_N \\
 &= -Nk_B T [\ln(n_Q V) + 1 - \ln N] \\
 &= -Nk_B T \left[\ln\left(\frac{n_Q V}{N}\right) + 1 \right] \\
 &= -Nk_B T \ln\left(\frac{n_Q}{n}\right) - Nk_B T \\
 &= -Nk_B T \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + 1 \right]
 \end{aligned}$$

since

$$\ln\left(\frac{n_Q V}{N}\right) = \ln\left[\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} \frac{V}{N}\right] = \ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + 1$$

The entropy S is obtained as

$$\begin{aligned}
 S &= -\left(\frac{\partial F}{\partial T}\right)_V \\
 &= Nk_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln\left(\frac{mk_B}{2\pi\hbar^2}\right) + \frac{5}{2} \right] \\
 &= Nk_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0 \right)
 \end{aligned}$$

where

$$\sigma_0 = \frac{5}{2} + \frac{3}{2} \ln\left(\frac{mk_B}{2\pi\hbar^2}\right)$$

Note that S can be rewritten as

$$S = Nk_B \ln \frac{n_Q}{n} + \frac{5}{2} Nk_B \quad (\text{Sackur-Tetrode equation})$$

((Sackur-Tetrode equation))

The Sackur–Tetrode equation is named for [Hugo Martin Tetrode](#) (1895–1931) and [Otto Sackur](#) (1880–1914), who developed it independently as a solution of Boltzmann's gas statistics and entropy equations, at about the same time in 1912.

https://en.wikipedia.org/wiki/Sackur%E2%80%93Tetrode_equation

In the classical region ($\frac{n}{n_Q} \ll 1$ or $\frac{n_Q}{n} \gg 1$), we have

$$\ln \frac{n_Q}{n} > 0$$

The internal energy E is given by

$$\begin{aligned} E &= F + ST \\ &= -Nk_B T \ln\left(\frac{n_Q}{n}\right) - Nk_B T + Nk_B T \ln \frac{n_Q}{n} + \frac{5}{2} Nk_B T \\ &= \frac{3}{2} Nk_B T \end{aligned}$$

Note that E depends only on T for the ideal gas (Joule's law). The factor $3/2$ arises from the exponent of T in n_Q because the gas is in 3D. If n_Q were in 1D or 2D, the factor would be $1/2$ or 2 , respectively.

(c) Pressure P

The pressure P is defined by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V}$$

leading to the Boyle's law. Then PV is

$$PV = Nk_B T = \frac{2E}{3} \quad (\text{Bernoulli's equation})$$

(d) Heat capacity

The heat capacity at fixed volume V is given by

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2} Nk_B.$$

When $N = N_A$, we have

$$C_V = \frac{3}{2} R.$$

C_p is the heat capacity at constant P . Since

$$dE = TdS - PdV$$

or

$$TdS = dE + PdV$$

then we get

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

$$P \left(\frac{\partial V}{\partial T} \right)_p = P \frac{N_A k_B}{P} = N_A k_B = R$$

We note that

$$E = \frac{3}{2} N_A k_B T.$$

E is independent of P and V , and depends only on T . (Joule's law)

$$\left(\frac{\partial E}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} N_A k_B = C_V$$

Thus we have

$$C_p = C_V + R = \frac{3}{2} R + R = \frac{5}{2} R.$$

((Mayer's relation))

$$C_p = C_V + R \quad \text{for ideal gas with 1 mole.}$$

The ratio γ is defined by

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3}.$$

(e) Isentropic process (constant entropy)

The entropy S is given by

$$S = Nk_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0 \right) = Nk_B [\ln(VT^{3/2}) - \ln N + \sigma_0]$$

The isentropic process is described by

$$VT^{3/2} = \text{const}, \quad \text{or} \quad TV^{2/3} = \text{const},$$

Using the Boyle's law ($PV = RT$), we get

$$\frac{PV}{R} V^{2/3} = \text{const}, \quad \text{or} \quad PV^{5/3} = \text{const}$$

Since $\gamma = 5/3$, we get the relation

$$PV^\gamma = \text{constant}$$

14. The expression of entropy: $S = k_B \ln W(E)$

The entropy is related to the number of states. It is in particular, closely related to $\ln W$. In order to find such a relation, we start with the partition function

$$Z = \sum_{\alpha} \exp(-\beta \varepsilon_{\alpha}) = \int dE W(E) \exp(-\beta E) = \int \exp[-N\beta f] dE$$

where $W(E)$ is the number of states with the energy E . The function $f(E)$ is defined by

$$f(E) = \frac{\beta E - \ln W(E)}{N\beta} = \frac{E - T k_B \ln W(E)}{N}$$

In the large limit of N , $f(E)$ is expanded using the Taylor expansion, as

$$f(E) = f(E^*) + \left. \frac{\partial f(E)}{\partial E} \right|_{E=E^*} (E - E^*) + \dots$$

where

$$\left. \frac{\partial f(E)}{\partial E} \right|_{E=E^*} = \frac{1}{N} \left[1 - k_B T \frac{\partial \ln W(E)}{\partial E} \right] = 0 \quad \text{at } E = E^*$$

or

$$\frac{1}{T} = k_B \left. \frac{\partial \ln W(E)}{\partial E} \right|_{E=E^*}$$

At at $E = E^*$,

$$Z = \exp[-N\beta f(E^*)]$$

For simplicity, we use E instead of E^* . The Helmholtz free energy F is defined by

$$F = -k_B T \ln Z = -k_B T [-N \beta f(E)] = N f(E)$$

or

$$F = E - k_B T \ln W(E) = E - ST$$

leading to the expression of the entropy S as

$$S = k_B \ln W(E),$$

and

$$\frac{1}{T} = \frac{\partial S}{\partial E}.$$

15. The expression of entropy: $S = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha}$

We consider the probability given by

$$p_{\alpha} = \frac{1}{Z} e^{-\beta E_{\alpha}},$$

where

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}},$$

$$\ln p_{\alpha} = -\ln Z - \beta E_{\alpha},$$

The energy E is given by

$$\begin{aligned} E &= \sum_{\alpha} p_{\alpha} E_{\alpha} \\ &= \frac{1}{Z} \sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta} \ln Z \end{aligned}$$

The entropy is a logarithmic measure of the number of states with significant probability of being occupied. The Helmholtz energy F is defined by

$$F = E - ST = -k_B T \ln Z .$$

The entropy S is obtained as

$$S = \frac{E - F}{T} = k_B \ln Z + \frac{E}{T}$$

We note that

$$\begin{aligned} -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha} &= -k_B \sum_{\alpha} p_{\alpha} (-\ln Z - \beta \varepsilon_{\alpha}) \\ &= k_B (\beta E + \ln Z) \\ &= \frac{E}{T} + \frac{k_B T}{T} \ln Z \\ &= \frac{E - F}{T} \\ &= S \end{aligned}$$

Thus it follows that the entropy S is given by

$$S = -k_B \sum_{\alpha} p_{\alpha} \ln p_{\alpha} .$$

16. Thermal average of energy fluctuation

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \sum_{\alpha} E_{\alpha}^2 e^{-\beta E_{\alpha}} - \frac{1}{Z^2} \left(\sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} \right)^2$$

$$\begin{aligned} \frac{d}{dT} \langle E \rangle &= \frac{d\beta}{dT} \frac{d}{d\beta} \langle E \rangle \\ &= -\frac{1}{k_B T^2} \frac{d}{d\beta} \langle E \rangle \\ &= -\frac{1}{k_B T^2} \frac{d}{d\beta} \left[\frac{1}{Z} \sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} \right] \\ &= -\frac{1}{k_B T^2} \frac{1}{Z^2} \left[Z \sum_{\alpha} (-E_{\alpha}^2) e^{-\beta E_{\alpha}} - \frac{dZ}{d\beta} \sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} \right] \\ &= \frac{1}{k_B T^2} [\langle E^2 \rangle - \langle E \rangle^2] \end{aligned}$$

where

$$\frac{dZ}{d\beta} = -\sum_{\alpha} E_{\alpha} e^{-\beta E_{\alpha}} = -Z \langle E \rangle$$

Then we have

$$\frac{d}{dT} \langle E \rangle = \frac{1}{k_B T^2} [\langle E^2 \rangle - \langle E \rangle^2]$$

Since $\frac{d}{dT} \langle E \rangle = C_V$, we get the relation

$$\frac{C_V}{k_B} = \frac{1}{(k_B T)^2} [\langle E^2 \rangle - \langle E \rangle^2]$$

17. Example: ${}^4\text{He}$ atom as ideal gas
We consider the ${}^4\text{He}$ atom with mass

$$m = 4u = 6.64216 \times 10^{-24} \text{ g}$$

The number density n at $P = 1 \text{ atm}$ and $T = 300 \text{ K}$, is

$$n = 2.44631 \times 10^{19} / \text{cm}^3$$

The number of atoms in the volume $V = 10^3 \text{ cm}^3$ is

$$N = nV = 2.44631 \times 10^{22}$$

The internal energy

$$E = \frac{3}{2} N k_B T = 151.987 \text{ J}$$

The entropy S

$$S = N k_B \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{m k_B}{2\pi \hbar^2} \right) + \frac{5}{2} \right] = 5.125 \text{ J/K.}$$

((**Mathematica**))

```
Clear["Global`*"];  
rule1 = {kB → 1.3806504 × 10-16,  
  NA → 6.02214179 × 1023,  
  ħ → 1.054571628 × 10-27,  
  amu → 1.660538782 × 10-24,  
  atm → 1.01325 × 106, bar → 106, J → 107};
```

```
n1 = 2.44631 × 1019; v1 = 103; T1 = 300;
```

```
N1 = n1 v1
```

```
2.44631 × 1022
```

```
m1 = 4 amu /. rule1
```

```
6.64216 × 10-24
```

```
P1 =  $\frac{\text{kB } N1}{v1} T1$  /. rule1
```

```
1.01325 × 106
```

P1 / bar / . rule1

1.01325

$$\mathbf{E1} = \frac{3}{2} \mathbf{kB} \mathbf{N1} \mathbf{T1} / . \mathbf{rule1}$$

1.51987×10^9

E1 / J / . rule1

151.987

$$\mathbf{S1} = \mathbf{kB} \mathbf{N1} \left(\frac{3}{2} \text{Log}[\mathbf{T1}] + \text{Log} \left[\frac{\mathbf{V1}}{\mathbf{N1}} \right] + \frac{3}{2} \text{Log} \left[\frac{\mathbf{m1} \mathbf{kB}}{2 \pi \hbar^2} \right] + \frac{5}{2} \right) / . \mathbf{rule1}$$

5.12503×10^7

S1 / J / . rule1

5.12503

17. Link

Entropy (Wikipedia)

[http://en.wikipedia.org/wiki/Entropy_\(statistical_thermodynamics\)](http://en.wikipedia.org/wiki/Entropy_(statistical_thermodynamics))

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APPENDIX

Density of states for N particles for micro-canonical ensemble

Using the density of states for the 1-particle system, the density of states for the 2-particle system is estimated as

$$\begin{aligned}
D_2(E_2) &= \int_0^{E_2} D_1(\varepsilon_1) D_1(E_2 - \varepsilon_1) d\varepsilon_1 \\
&= C^2 \int_0^{E_2} \sqrt{\varepsilon_1} \sqrt{E_2 - \varepsilon_1} d\varepsilon_1 \\
&= C^2 E_2^2 \int_0^1 \sqrt{x} \sqrt{1-x} dx = C^2 E_2^2 f(2)
\end{aligned}$$

where E_2 is the total energy of two-particle system, and

$$f(n) = \int_0^1 x^{1/2} (1-x)^{3(n-1)/2-1} dx = \frac{\Gamma(\frac{3}{2}) \Gamma[\frac{3}{2}(n-1)]}{\Gamma(\frac{3}{2}n)}$$

Similarly, the density of states for the 3-particle system is

$$\begin{aligned}
D_3(E_3) &= \int_0^{E_3} D_1(\varepsilon_1) D_2(E_3 - \varepsilon_1) d\varepsilon_1 \\
&= C^3 f(2) \int_0^{E_3} \sqrt{\varepsilon_1} (E_3 - \varepsilon_1)^2 d\varepsilon_1 \\
&= C^3 E_3^{7/2} \int_0^1 \sqrt{x} (1-x)^2 dx \\
&= C^3 E_3^{7/2} f(2) f(3)
\end{aligned}$$

where E_3 is the total energy of three particles.

Suppose that D_n has the form

$$D_n(E_n) = C^n f(2)f(3)\dots f(n)E_n^{3(n-1)/2+1/2}$$

then Ω_{n+1} can be described as

$$\begin{aligned} D_{n+1}(E_{n+1}) &= C^{n+1} f(2)f(3)\dots f(n) \int_0^{E_{n+1}} C \sqrt{\varepsilon_1} (E_{n+1} - \varepsilon_1)^{3(n-1)/2+1/2} d\varepsilon_1 \\ &= C^{n+1} f(2)f(3)\dots f(n)f(n+1)E_{n+1}^{3n/2+1/2} \end{aligned}$$

Hence the density of states for the N -particles system is given by

$$D_N(E) = C^N f(2)f(3)\dots f(N)E^{3(N-1)/2+1/2}$$

where $E = E_N$

$$\begin{aligned} f(2)f(3)\dots f(N) &= \frac{\Gamma(\frac{3}{2})\Gamma[\frac{3}{2}]\Gamma(\frac{3}{2})\Gamma[3]\Gamma(\frac{3}{2})\Gamma[\frac{9}{2}]}{\Gamma(3)\Gamma(\frac{9}{2})\Gamma(\frac{12}{2})\dots} \frac{\Gamma(\frac{3}{2})\Gamma[\frac{3}{2}(N-2)]\Gamma(\frac{3}{2})\Gamma[\frac{3}{2}(N-1)]}{\Gamma(\frac{3}{2}(N-1))\Gamma(\frac{3}{2}N)} \\ &= \frac{[\Gamma(\frac{3}{2})]^N}{\Gamma(\frac{3N}{2})} \end{aligned}$$

One can get

$$\begin{aligned} D_N(E) &= C^N \frac{[\Gamma(\frac{3}{2})]^N}{\Gamma(\frac{3N}{2})} E^{3(N-1)/2+1/2} \\ &= \frac{V^N}{(4\pi^2\hbar^3)^N} (2m)^{3N/2} \frac{[\Gamma(\frac{3}{2})]^N}{\Gamma(\frac{3N}{2})} E^{3N/2} \frac{1}{E} \\ &= \frac{V^N}{(4\pi^2\hbar^3)^N} \frac{1}{2^N} (2m)^{3N/2} \frac{\pi^{N/2}}{\Gamma(\frac{3N}{2})} E^{3N/2} \frac{1}{E} \end{aligned}$$

where

$$\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$$

The number of states whose energy lies between E and $E + \delta E$ is given by

$$\begin{aligned} W(E, \delta E) &= \frac{1}{N!} D_N(E) \delta E \\ &= \frac{1}{N!} \frac{V^N}{(4\pi^2 \hbar^3)^N} \frac{1}{2^N} (2m)^{3N/2} \frac{\pi^{N/2}}{\Gamma(\frac{3N}{2})} E^{3N/2} \frac{\delta E}{E} \end{aligned}$$

where $N!$ is included because N -particles are non-distinguishable.

This can be rewritten as

$$W(E, \delta E) = \frac{V^N}{N! \Gamma(3N/2)} \left(\frac{mE}{2\pi\hbar^2} \right)^{3N/2} \frac{\delta E}{E},$$

which is exactly the same as the expression derived from the classical approach.