**Canonical ensemble**
Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date: September 06, 2018)

Here we discuss the method of canonical ensemble, which is much simpler than that of microcanonical ensemble. We show that both methods are equivalent. In other words, the same results are derived using two methods.

1.   Thermal equilibrium

We consider the number of accessible states of two systems in thermal contact, with constant total energy,

$$E = E_1 + E_2$$
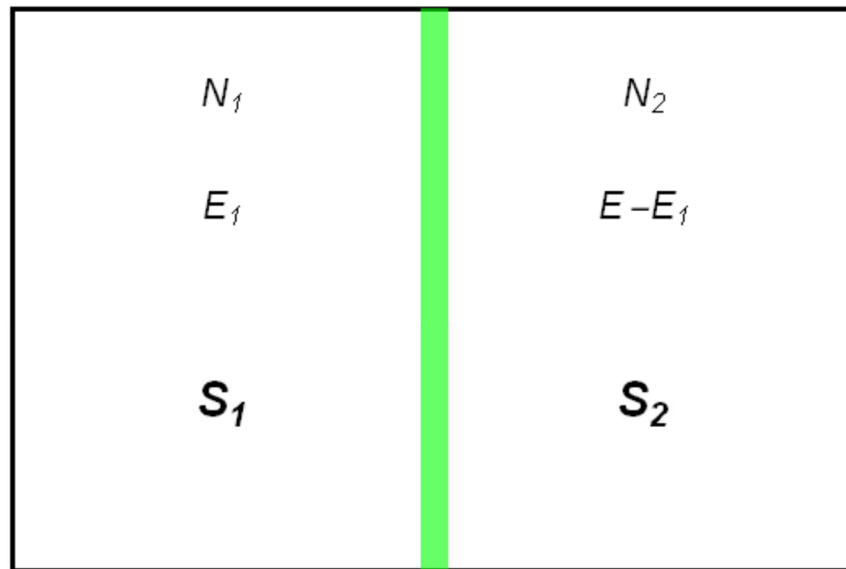
Thermal contact

The multiplicity $g(N, E)$ of the combined system is

$$g(N,E) = \sum_{E_1 \le E} g_1(N_1, E_1) g_2(N_2, E - E_1)$$

The largest term in $g(N, E)$ governs the properties of the total system in thermal equilibrium. For an extremum, it is necessary that the differential of $g(N, E)$ be zero for an infinitesimal change of energy.

$$dg = \left(\frac{\partial g_1}{\partial E_1}\right)_{N_1} g_2 dE_1 + g_1 \left(\frac{\partial g_2}{\partial E_2}\right)_{N_2} dE_2 = 0$$

$$dE_1 + dE_2 = 0$$

The thermal equilibrium condition is

$$\frac{1}{g_1}\left(\frac{\partial g_1}{\partial E_1}\right)_{N_1} = \frac{1}{g_2}\left(\frac{\partial g_2}{\partial E_2}\right)_{N_2}$$

which may be written as

$$\left(\frac{\partial \ln g_1}{\partial E_1}\right)_{N_1} = \left(\frac{\partial \ln g_2}{\partial E_2}\right)_{N_2}. \qquad (1)$$

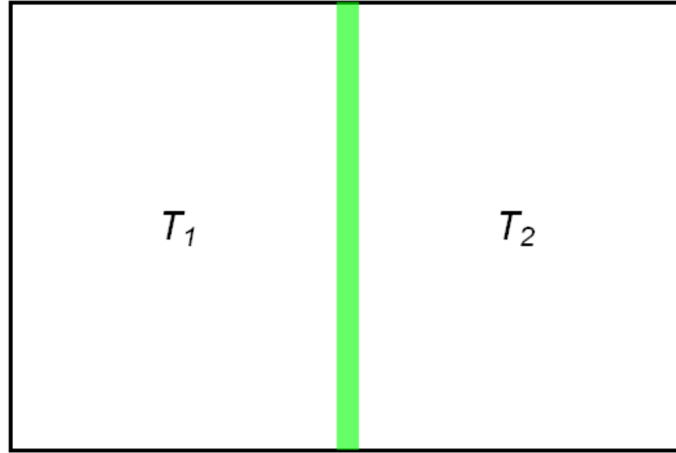We define the entropy S as

$$S(N,E) = k_B \ln g(N,E)$$

We write Eq.(1) in the final form

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{N_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{N_2}$$

This is the condition for thermal equilibrium for two systems in thermal contact.

2. Temperature

The last equality leads to us to the concept of temperature. In thermal equilibrium, the temperature of the two systems are equal.

$$T_1 = T_2$$

This rule must be equivalent to

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{N_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{N_2}$$

$$\frac{1}{T} = \frac{\partial(S,N)}{\partial(E,N)} = \frac{1}{\frac{\partial(E,N)}{\partial(S,N)}} = \frac{1}{\left(\frac{\partial E}{\partial S}\right)_N}$$

or

$$T = \left(\frac{\partial E}{\partial S}\right)_N$$

So that T must be a function of $\left(\frac{\partial S}{\partial E}\right)_N$. If T denotes the absolute temperature in K, this function is simply the inverse relationship,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N.$$

((Note))

What is the difference between the expression

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N \qquad\qquad (1)$$

and the expression

$$T = \left(\frac{\partial E}{\partial S}\right)_N . \qquad\qquad (2)$$

These two expressions have a slightly different meaning. In Eq.(1), S is given as a function of the independent variables E and N as $S(E,N)$. Hence T has the same independent variables $T = T(E,N)$. In Eq.(2), $E = E(S,N)$. So that $T = T(S,N)$. The definition of temperature is the same in both cases, but it is expressed as a function of different independent variables.

REFERENCES
C. Kittel and H. Kroemer, second edition (W.H. Freeman and Company, 1980).
D.S. Lemons, Mere Thermodynamics, second edition (The John Hopkins University Press, 2009).

3.   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 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.
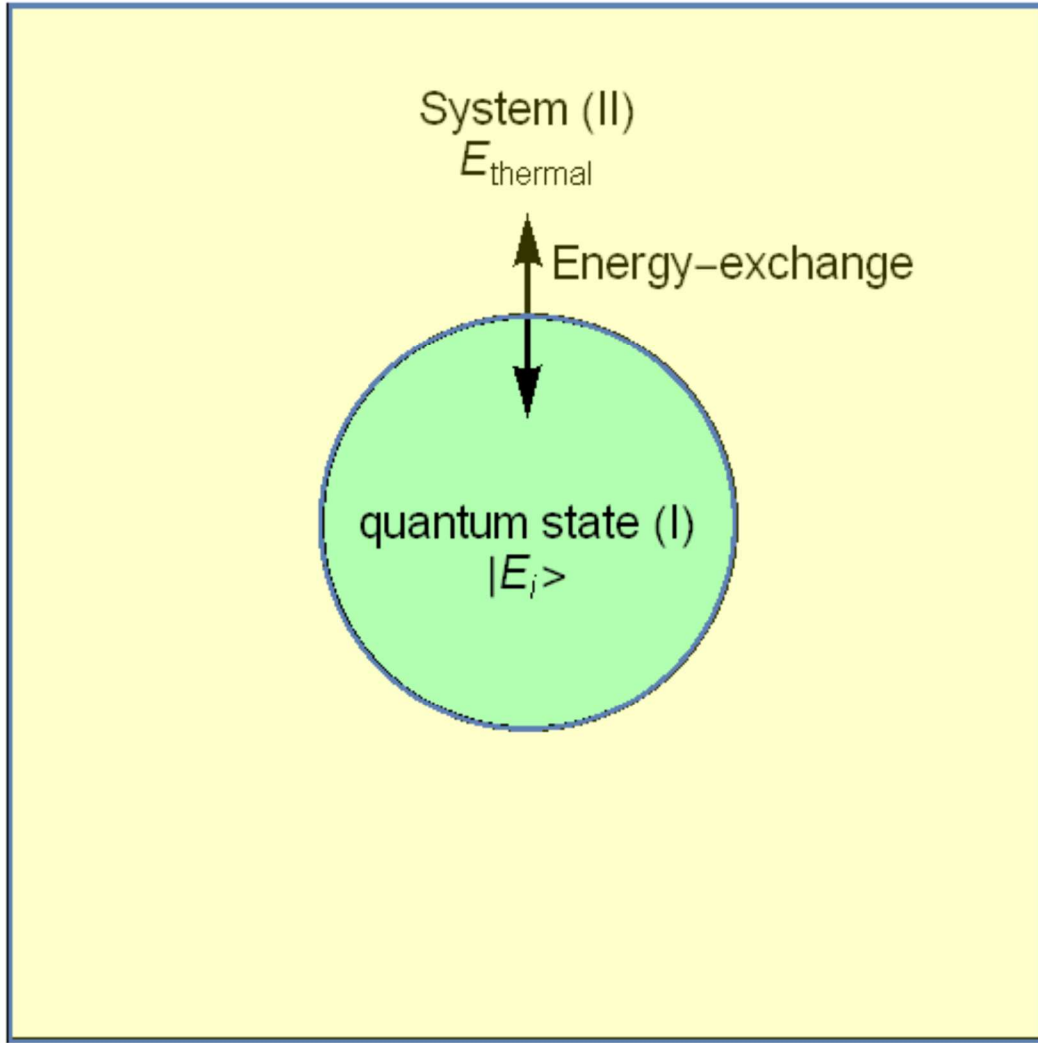
Fig. System one (one quantum state) and system II (thermal bath, reservoir).

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

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

Since

$$E_T >> E_i$$

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

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

((**Note**))   Taylor expansion

$$f(x) = \ln[W_{II}(E_{II})] = \ln[W_{II}(E_T - E_i)] = \ln[W_{II}(E_T - x)]$$

with

$$x = E_i \ll E_T$$

$$f(x) = f(0) + \frac{x}{1!}\frac{\partial f}{\partial x}\Big|_{x \to 0}$$
$$= \ln[W_{II}(E_T)] - \frac{\partial \ln[W_{II}(E_{II})]}{\partial E_{II}}\Big|_{E_T} E_i$$

where

$$f(0) = \ln[W_{II}(E_T)]$$

$$\frac{\partial f}{\partial x} = \frac{\partial E_{II}}{\partial x}\frac{\partial}{\partial E_{II}}\ln[W_{II}(E_{II})]$$
$$= \frac{\partial E_{II}}{\partial E_i}\frac{d}{dE_{II}}\ln[W_{II}(E_{II})]$$
$$= -\frac{\partial \ln[W_{II}(E_{II})]}{\partial E_{II}}$$

Then we obtain

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

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

$$\frac{d \ln W_{II}(E_{II})}{dE_{II}} = \frac{1}{k_B}\frac{\partial S_{II}}{\partial E_{II}} = \frac{1}{k_B T_{II}}$$

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

$$Z_C(\beta) = \sum_i e^{-\beta E_i}$$
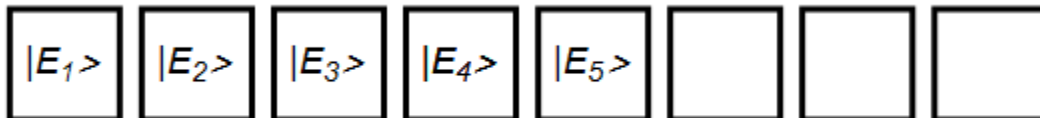
Quantum mechanical approach

Fig. Canonical ensemble

Here we use the quantum mechanical description to explain the canonical ensemble.

$$\hat{H}|i\rangle = E_i|i\rangle \qquad \text{(Eigenstate in the quantum mechanics, quantum state)}$$

The probability is given by

$$p_i = |\langle i|\psi\rangle|^2$$

where $\hat{H}$ is the Hamiltonian of the system. The letter Z_C is used because the German name is "==Zustandssumme.==" (sum over states). The probability is expressed by

$$p(E_i) = \frac{1}{Z_C}e^{-\beta E_i}$$

The summation in Z_C 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

$$U = \langle E\rangle = \frac{1}{Z_C}\sum_i E_i e^{-\beta E_i} = -\frac{\partial \ln Z_C}{\partial \beta}$$

since

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

Note that

$$U = -\frac{\partial \ln Z_C}{\partial \beta} = -\frac{1}{\dfrac{\partial \beta}{\partial T}}\frac{\partial \ln Z_C}{\partial T} = k_B T^2 \frac{\partial \ln Z_C}{\partial T}.$$

since

$$\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = \frac{1}{\dfrac{\partial \beta}{\partial T}}\frac{\partial}{\partial T} = -k_B T^2$$

In summary, the representative points of the system I are distributed with the probability density proportional to exp(-βE_i). This is called the ==canonical ensemble==, and this distribution of

representative points is called the canonical distribution. The factor exp(-βE_i) is often referred to as the Boltzmann factor. The energy E_i is dependent on T.

((Note)) R. Baierlein Thermal Physics

$$p(E_i) = \frac{1}{Z_C} e^{-\beta E_i}$$

This probability distribution, perhaps the most famous in all of thermal physics, is called the canonical probability distribution, name introduced by J. Willard Gibbs in 1901. (The adjective "canonical" is used in the sense of "standard.)

((**Example**)) **Blundel-Blundell Problem 4-3**
Blunde-Blundell Problem 4-3

(4.3) A system comprises N states which can have energy 0 or Δ. Show that the number of ways $\Omega(E)$ of arranging the total system to have energy $E = r\Delta$ (where r is an integer) is given by

$$\Omega(E) = \frac{N!}{r!(N-r)!}. \qquad (4.33)$$

Now remove a small amount of energy $s\Delta$ from the system, where $s \ll r$. Show that

$$\Omega(E - \epsilon) \approx \Omega(E)\frac{r^s}{(N-r)^s}, \qquad (4.34)$$

and hence show that the system has temperature T given by

$$\frac{1}{k_B T} = \frac{1}{\Delta} \ln\left(\frac{N-r}{r}\right). \qquad (4.35)$$

Sketch $k_B T$ as a function of r from $r = 0$ to $r = N$ and explain the result.

((**Solution**))
   We consider the two states with energy 0 and energy Δ. Suppose that the system consists of N particles. Each particle takes one of these two energy states.

$$N = N_1 + N_2$$

The total energy of the system is

$$E = 0N_1 + \Delta N_2 = r\Delta$$

Then we have

$$N_2 = r, \qquad N_1 = N - r$$

The number of ways is

$$\Omega(E = r\Delta) = \Omega(r\Delta) = \frac{N!}{(N-r)!r!}$$

For small amount of $\varepsilon = s\Delta$ $(s \ll r)$

$$\Omega(E - \varepsilon) = \Omega[(r-s)\Delta]$$

$$= \frac{N!}{(N-r+s)!(r-s)!}$$

$$= \Omega(E = r\Delta)\frac{N!}{(N-r+s)!(r-s)!}\frac{(N-r)!r!}{N!}$$

$$= \Omega(E = r\Delta)\frac{(N-r)!r!}{(N-r+s)!(r-s)!}$$

$$= \Omega(E = r\Delta)\frac{(r-1)(r-2)....(r-s+1)}{(N-r+1)(N-r+2)...(N-r+s)}$$

$$\approx \Omega(E = r\Delta)\frac{r^s}{(N-r)^s}$$

or

$$\Omega(E - \varepsilon) = \Omega(E)\exp[-\frac{\varepsilon}{\Delta}\ln\left(\frac{N-r}{r}\right)] \tag{1}$$

Note that

$$X = \frac{r^s}{(N-r)^s},$$

$$\ln X = s \ln r - s \ln(N - r)$$

$$= -s \ln\left(\frac{N-r}{r}\right)$$

leading to the expression

$$X = \exp\left[-s \ln\left(\frac{N-r}{r}\right)\right] = \exp\left[-\frac{\varepsilon}{\Delta} \ln\left(\frac{N-r}{r}\right)\right]$$

Using the Taylor expansion, we have

$$\ln\Omega(E - \varepsilon) = \ln\Omega(E) - \frac{d\ln\Omega(E)}{dE}\varepsilon = \ln\Omega(E) - \frac{\varepsilon}{k_B T}$$

or

$$\Omega(E - \varepsilon) = \Omega(E)\exp\left(-\frac{\varepsilon}{k_B T}\right) \qquad (2)$$

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

$$\frac{1}{k_B T} = \frac{1}{\Delta}\ln\left(\frac{N-r}{r}\right)$$

or

$$y = \frac{k_B T}{\Delta} = \frac{1}{\ln\left(\frac{N-r}{r}\right)} = \frac{1}{\ln\left(\frac{1-x}{x}\right)}$$

with

$$x = \frac{r}{N}.$$

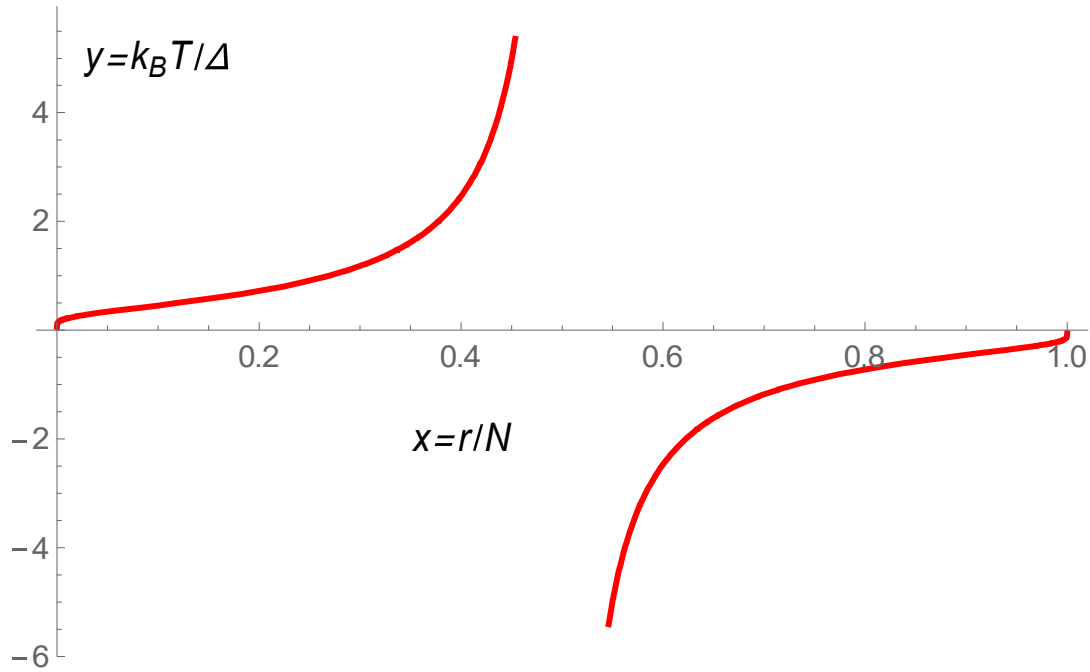Using the Mathematica, we make a plot of y as a function of x.

$y = k_B T / \Delta$

$x = r/N$

Fig. Plot of $y = \dfrac{k_B T}{\Delta}$ as s function of $x = \dfrac{r}{N}$.

---

4. Canonical ensemble: Boltzmann factor
(Kittel, Thermal Physics)

We consider the case of a small system S in thermal interaction with a heat reservoir R. We assume that the system S is in thermal equilibrium with a reservoir R. S and R have a common temperature T (given). The total system $(R+S)$ is a closed system. We assume weak interaction between R and S. So that their energies are additive. The energy of the system S is, of course, not fixed. The total energy of the combined system $(R+S)$ is constant E_0. The energy conservation can be written as

$$E_R + E = E_{total}$$
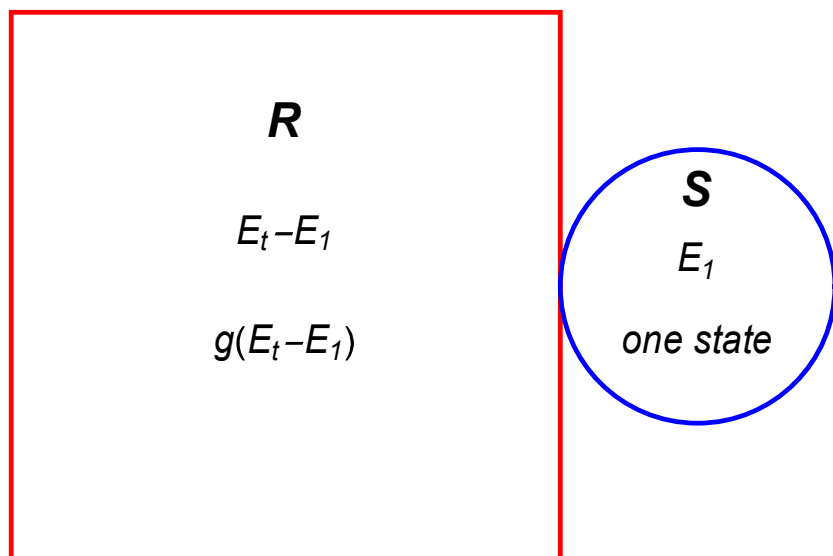
The system is in a quantum state 1, and the reservoir **R** has

$$g_R(E_t - E_1)$$

states accessible to it. The system is in a quantum state 2, and the reservoir **R** has

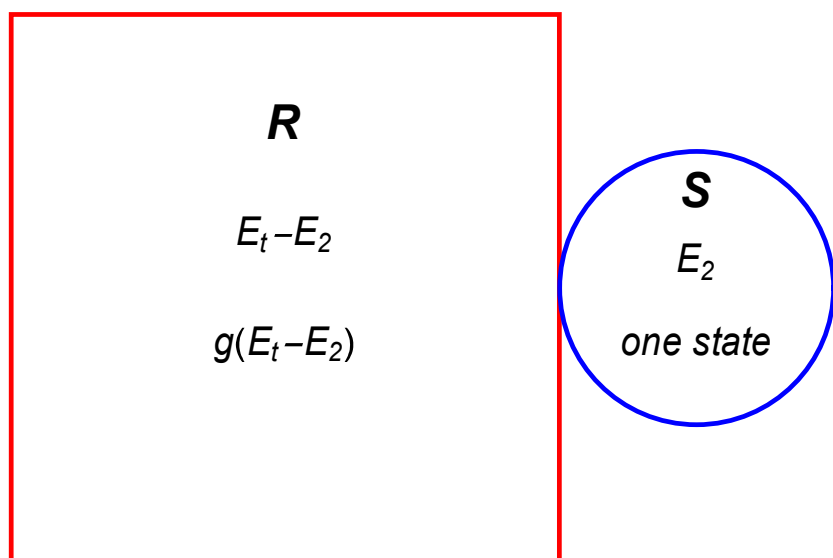$$g_R(E_t - E_2)$$

states accessible to it.

Fig.   The system is in quantum state $|E_1\rangle$. The reservoir has $g_R(E_t - E_1)$ accessible quantum states

The probability $P(E)$ is proportional to the number of accessible states of the reservoir when the state of the system is exactly specified. If we specify the state of S, the number of accessible states of R:

$$g(R + S) = g(R) \times 1$$

Thus the probability $P(E_s)$ is proportional to the number of accessible states of the reservoir,

$$P(E_s) \propto g_R(E_t - E_s).$$

Thus

$$\frac{P(E_1)}{P(E_2)} = \frac{g_R(E_t - E_1)}{g_R(E_t - E_2)}.$$

By definition of entropy,

$$S_R(E_t - E_1) = k_B \ln[g_R(E_t - E_1)]$$

$$S_R(E_t - E_2) = k_B \ln[g_R(E_t - E_2)]$$

So that the probability ratio may be written as

$$\frac{P(E_1)}{P(E_2)} = \frac{\exp[\frac{1}{k_B} S_R(E_t - E_1)]}{\exp[\frac{1}{k_B} S_R(E_t - E_2)]} = \exp[\frac{1}{k_B} \Delta S_R].$$

Here the entropy difference ΔS_R is

$$\Delta S_R = S_R(E_t - E_1) - S_R(E_t - E_2)$$

$$= S_R(E_t) - \left(\frac{\partial S_R}{\partial E_t}\right)E_1$$

$$-[S_R(E_t) - \left(\frac{\partial S_R}{\partial E_t}\right)E_2]$$

$$= -(E_1 - E_2)\left(\frac{\partial S_R}{\partial E_t}\right)$$

We know that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E_t}\right).$$

Then the entropy difference is

$$\Delta S_R = -\frac{(E_1 - E_2)}{T}.$$

Finally we have

$$\frac{P(E_1)}{P(E_2)} = \frac{\exp(-\beta E_1)}{\exp(-\beta E_2)}.$$

with

$$\beta = \frac{1}{k_B T}.$$

A term of $\exp(\frac{-E}{k_B T})$ is called a Boltzmann factor. It gives the ratio of the probability of finding the system in a single quantum state $|E_1\rangle$ to the probability of finding the system in a single quantum state $|E_2\rangle$.

5. Pressure
The pressure P is defined as

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

Here we define the Helmholtz free energy F as

$$F = E - ST.$$

$$dF = dE - SdT - TdS$$
$$= TdS - PdV - SdT - TdS$$
$$= -PdV - SdT$$

F is a function of T and V; $F = F(T, V)$. From the equation of dF, we have

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

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

((**Note**))   Notation A for the Helmholtz free energy

The Helmholtz free energy was developed by Hermann von Helmholtz, a German physicist, and is usually denoted by the letter A (from the German "Arbeit" or work), or the letter F. The IUPAC recommends the letter A as well as the use of name *Helmholtz energy*.

6.   **Helmholtz free energy and entropy**
    The Helmholtz free energy F is given by

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

((**Proof**))
We note that

$$\frac{\partial}{\partial T}(\frac{F}{T}) = \frac{T\frac{\partial F}{\partial T} - F}{T^2} = \frac{-ST - F}{T^2} = -\frac{U}{T^2} = -k_B \frac{\partial}{\partial T} \ln Z_C,$$

which leads to

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

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

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

where U is the average energy of the system,

$$U = -\frac{\partial \ln Z_C}{\partial \beta}$$

Then entropy S is rewritten as

$$S = -\frac{1}{T}\frac{\partial \ln Z_C}{\partial \beta} + k_B \ln Z_C$$

$$= \frac{1}{T}\frac{1}{Z_C}\sum_i E_i e^{-\beta E_i} + k_B \ln Z_C$$

$$= k_B \beta \sum_i E_i \frac{e^{-\beta E_i}}{Z_C} + k_B \ln Z_C$$

$$= k_B \sum_i \beta E_i p_i + k_B \ln Z_C$$

$$= k_B \sum_i (-\ln p_i - \ln Z_C)p_i + k_B \ln Z_C$$

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

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

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

The logarithm of p_i is described by

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

Here we have

$$S = -k_B \sum_i p_1 \ln p_i = -k_B \sum_i p_1 (-\beta E_i - \ln Z_C)$$
$$= -k_B (-\beta U - \ln Z_C)$$
$$= \frac{U}{T} + k_B \ln Z_C$$

or

$$TS = U + k_B T \ln Z_C$$

or

$$F = U - ST = -k_B T \ln Z_C$$

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

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

((**Example**))
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.

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

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

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

$$p_1 = p_3 = ... = p_{49} = 0$$
$$p_2 = p_4 = ... = p_{50} = \frac{1}{25}$$

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

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

$p_{10}=1$
$p_s = 0$ $(s \neq 10)$

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

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

7. The method (Fermi)

I found very interesting method for the derivation of the expression entropy S and the Helmholtz free energy F in the book written by Enrico Fermi, one of the greatest scientists in the world.

E. Fermi, Notes on Thermodynamics and Statistics (University of Chicago, 1966).

According to his book, we start with the expression

$$dU = TdS - PdV = d(TS) - SdT - PdV$$

or

$$d(U - TS) = dF = -SdT - PdV$$

with

$$F = U - ST \qquad \text{or} \qquad S = \frac{U}{T} - \frac{F}{T}$$

Note that

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

At constant V, we get

$$dS = \frac{1}{T}dU = k_B \beta dU = k_B[d(\beta U) - Ud\beta]$$

Using the relation

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

we have

$$S = \int \frac{1}{T} dU$$

$$= \int k_B \beta \, dU$$

$$= \int k_B [d(\beta U) - U d\beta]$$

or

$$S = k_B \beta U + k_B \int \frac{\partial}{\partial \beta}(\ln Z) d\beta$$

$$= k_B \beta U + k_B \ln Z$$

$$= \frac{U}{T} + k_B \ln Z$$

or

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

The Helmholtz free energy is

$$F = -k_B T \ln Z = -\frac{1}{\beta} \ln Z$$

The entropy S is

$$S = k_B [\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z] = -k_B \beta^2 \frac{\partial}{\partial \beta}(\frac{1}{\beta} \ln Z)$$

This expression of S can be also derived as

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

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

$$= k_B \beta^2 \left(\frac{\partial F}{\partial \beta}\right)_V$$

$$= -k_B \beta^2 \frac{\partial}{\partial \beta}\left(\frac{1}{\beta} \ln Z\right)$$

7.   Application

7.1. Partition function Z_C for ideal gas system

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

$$Z_{CN} = \frac{V^N}{N! h^{3N}} [\int_{-\infty}^{\infty} dp \exp(-\frac{p^2}{2mk_BT})]^{3N}$$

$$= \frac{V^N}{N!} (\frac{2\pi mk_BT}{h^2})^{3N/2}$$

where $N!$ is a factor coming from indistinguishable particles (Gibbs paradox). Note that

$$Z_{CN} = \frac{1}{N!}(Z_{C1})^N .$$

Z_{C1} is the one-particle partition function.

$$Z_{C1} = \frac{V}{h^3} [\iiint dp_x dp_y dp_z \exp(-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_BT})$$

$$= \frac{V}{h^3} [\int_{-\infty}^{\infty} dp_x \exp(-\frac{p_x^2}{2mk_BT}) \int_{-\infty}^{\infty} dp_y \exp(-\frac{p_y^2}{2mk_BT}) \int_{-\infty}^{\infty} dp_z \exp(-\frac{p_z^2}{2mk_BT})]$$

$$= \frac{V}{h^3} [\int_{-\infty}^{\infty} dp_x \exp(-\frac{p_x^2}{2mk_BT})]^3$$

$$= V(\frac{2\pi mk_BT}{h^2})^{3/2}$$

In other words, many-particle problem reduces to one particle problem. Using this expression of Z_{CN}, the Helmholtz free energy F can be calculated as

$$F = -k_BT \ln Z_{CN} = Nk_BT[-\ln(\frac{V}{N}) - \frac{3}{2}\ln(\frac{2\pi mk_BT}{h^2}) - 1] .$$

The internal energy E is

$$U = -\frac{\partial \ln Z_{CN}}{\partial \beta} = \frac{3}{2} Nk_BT .$$

The entropy S is

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

The pressure P is

$$P = -(\frac{\partial F}{\partial V})_T = \frac{Nk_BT}{V}.$$ (Boyle's law).

or

$$PV = \frac{2}{3}U$$

7.2. Partition function Z_C for photon gas system

We consider the photon gas system with the energy dispersion $\varepsilon = cp$. The N-photon partition function is given by

$$Z_{CN} = \frac{1}{N!}(Z_{C1})^N.$$

Z_{C1} is the one-photon partition function and is given by

$$
\begin{aligned}
Z_{C1} &= \frac{V}{h^3}\int_0^\infty dp\, 4\pi p^2 e^{-\beta cp} \\
&= \frac{V}{h^3} 4\pi \frac{2!}{(\beta c)^3} \\
&= \frac{8\pi V}{(h\beta c)^3}
\end{aligned}
$$

the Helmholtz free energy F can be calculated as

$$
\begin{aligned}
F &= -k_BT \ln Z_{CN} \\
&= -k_BT \ln \frac{(Z_{C1})^N}{N!} = -Nk_BT[\ln\frac{V}{N} + 3\ln(k_BT) + \ln(\frac{8\pi}{h^3c^3}) + 1]
\end{aligned}
$$

where

$$\ln Z_{CN} = N[\ln\frac{V}{N} + 3\ln(k_BT) + \ln(\frac{8\pi}{h^3c^3}) + 1].$$

The internal energy E is

$$U = -\frac{\partial \ln Z_{CN}}{\partial \beta} = 3Nk_BT.$$

The pressure P is

$$P = -(\frac{\partial F}{\partial V})_T = \frac{Nk_BT}{V} . \qquad \text{(Boyle's law)}.$$

or

$$PV = \frac{1}{3}U .$$

7.3 Maxwell's distribution function

The Maxwell distribution function can be derived as follows.

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

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

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

Then we have

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

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

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

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

((**Mathematica**))

```
f1 = Integrate[Exp[(-m v²)/(2 kB T)] 4 π v², {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]
```

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

8. 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

$$Z_C = \sum_i e^{-\beta E_i} = \int \Omega(E)e^{-\beta E} dE$$

The partition function $Z_C(\beta)$ is the Laplace transform of the density of states, $\Omega(\varepsilon)$. The density of states $\Omega(\varepsilon)$ is related to the partition function $Z_C(\beta)$, through an inverse Laplace transform,
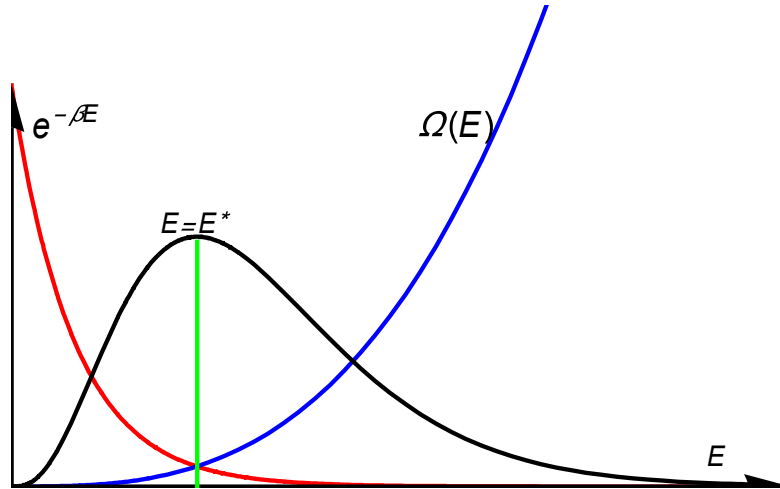
$$\Omega(E) = \frac{1}{2\pi i} \int_{\beta^*-i\infty}^{\beta^*+i\infty} e^{\beta E} Z_C(\beta) d\beta \qquad \text{(Bromwich-Wagner integral)}$$

where $\beta^* > 0$.

Here we define the function $\psi(E)$ by

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

The function $e^{-\beta E}$ decreases with increasing E while $\Omega(E)$ increases with increasing E.

We assume that $\psi(E)$ has a local maximum at $E = E^*$

$$\ln \psi(E) = \ln \psi(E^*) + (E - E^*) \frac{\partial \ln \psi(E)}{\partial E}\Big|_{E=E^*} + \frac{1}{2!}(E - E^*)^2 \frac{\partial^2 \ln \psi(E)}{\partial E^2}\Big|_{E=E^*} + \dots$$

We choose E^* and σ_E such that

$$\frac{\partial \ln \psi(E)}{\partial E}\Big|_{E=E^*} = 0, \qquad\qquad \frac{\partial^2 \ln \psi(E)}{\partial E^2}\Big|_{E=E^*} = -\frac{1}{2(\sigma_E)^2}$$

Thus we have

$$\ln \psi(E) = \ln \psi(E^*) - \frac{1}{2(\sigma_E)^2}(E - E^*)^2$$

$\psi(E)$ can be approximated by a Gaussian function

$$\psi(E) = \psi(E^*)\exp[-\frac{(E - E^*)^2}{2(\sigma_E)^2}]$$
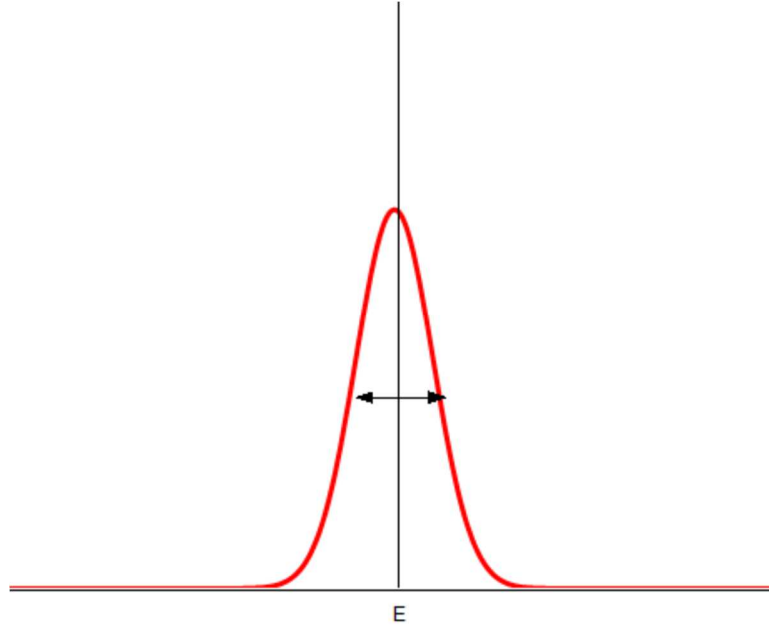
where

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

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

Since

$$\frac{d\ln\psi(E)}{dE} = \frac{d\ln\Omega(E)}{dE} - \beta$$

we have

$$\frac{d\ln\psi(E)}{dE}\Big|_{E=E^*} = \frac{d\ln\Omega(E)}{dE}\Big|_{E=E^*} - \beta = 0$$

or

$$\frac{d\ln\Omega(E)}{dE}\Big|_{E=E^*} = \beta$$

Here we define the number of states $W(E, \delta E)$ by

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

with

$$\delta E = \sqrt{2\pi}\sigma_E^*.$$

Then we have

$$\frac{d\ln W(E,\delta E)}{dE}\Big|_{E=E^*} = \beta \tag{1}$$

since

$$\ln W(E,\delta E) = \ln \Omega(E^*) + \ln \delta E$$

$$\frac{\partial \ln W(E,\delta E)}{\partial E}\Big|_{E=E^*} = \frac{\partial \ln \Omega(E)}{\partial E}\Big|_{E=E^*} = \beta$$

with fixed δE. We note that

$$Z_C = \int \psi(E)dE$$

$$= \psi(E^*)\int_0^\infty \exp[-\frac{(E-E^*)^2}{2(\sigma_E)^2}]dE$$

$$= \psi(E^*)\sqrt{2\pi}\sigma_E$$

$$= \sqrt{2\pi}\sigma_E \Omega(E^*)\exp(-\beta E^*)$$

where

$$\int_0^\infty \frac{1}{\sqrt{2\pi}\sigma_E}\exp[-\frac{(E-E^*)^2}{2(\sigma_E)^2}]dE = 1 \qquad \text{(Gaussian distribution)}$$

Then we have

$$\ln Z_C = \ln[\sqrt{2\pi}\sigma_E \Omega(E^*)] - \beta E^*$$

We note that

$$F = -k_B T \ln Z_C, \qquad E = E^* = -\frac{1}{Z_C}\frac{\partial Z_C}{\partial \beta} = -\frac{\partial \ln Z_C}{\partial \beta}$$

The entropy S is calculated as

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

$$= -\frac{1}{T}\frac{\partial \ln Z_C}{\partial \beta} + k_B \ln Z_C$$

$$= \frac{E^*}{T} + k_B \ln[\sqrt{2\pi}\sigma_E \Omega(E^*)] - \frac{E^*}{T} \tag{2}$$

$$= k_B \ln[\sqrt{2\pi}\sigma_E \Omega(E^*)]$$

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

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

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

or

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

In other words, the thermodynamic properties derived from the canonical ensemble is equivalent to those from the microcanonical ensemble. Since the calculations for the microcanonical ensemble is much more complicated compared to those for the canonical ensemble, it is suggest that one may choose the method of canonical ensemble if it is allowed.

((**Note-1**))   Expression for $\Omega(E)$

$$\psi(E) = e^{-\beta E^*}\Omega(E^*)\exp[-\frac{(E - E^*)^2}{2(\sigma_E)^2}] = e^{-\beta E}\Omega(E)$$

or

$$\Omega(E) = \Omega(E^*)\exp[\beta(E - E^*) - \frac{(E - E^*)^2}{2(\sigma_E)^2}]$$

This function takes a maximum at

$$E = E^* + \beta\sigma_E^2.$$

9.   Boltzmann-Planck's method
Finally we show the standard method of the derivation, which characterizes well the theory of canonical ensembles.
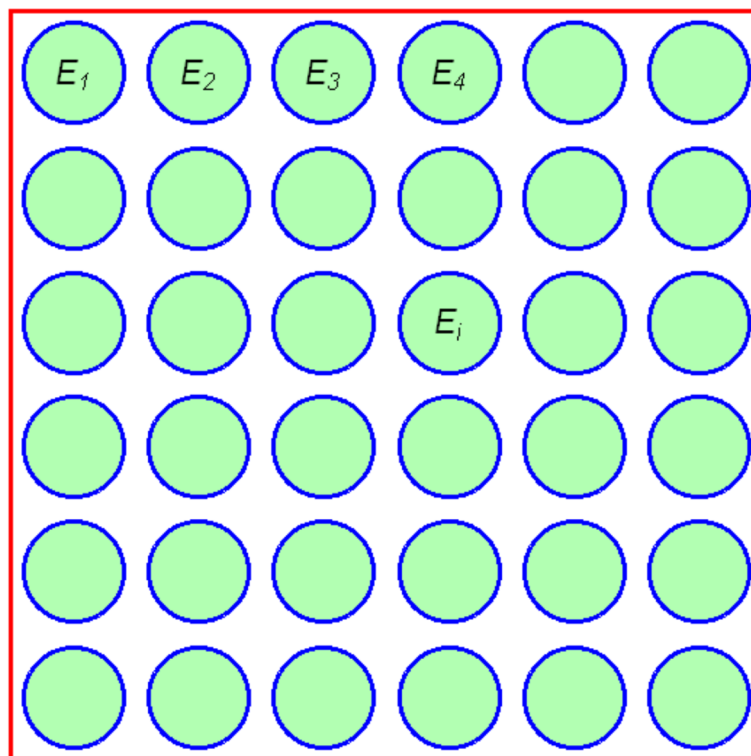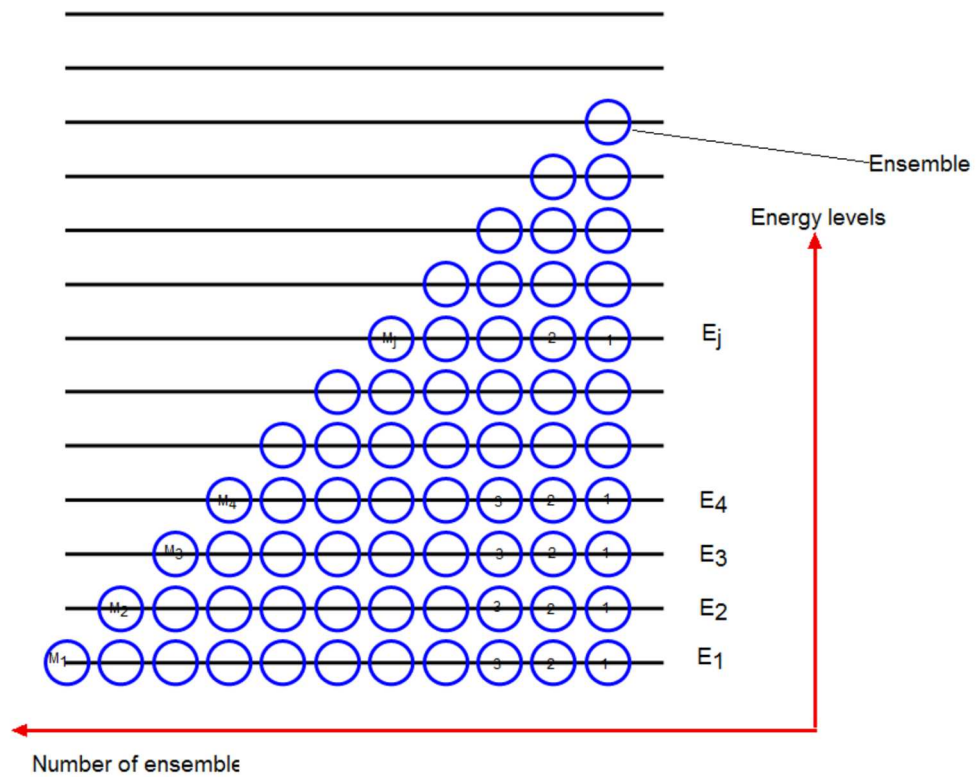
Ensemble

Energy levels

E_j

M_j 2   1

E_4

M_4 3   2   1

E_3

M_3 3   2   1

E_2

M_2 3   2   1

E_1

M_1 3   2   1

Number of ensemble

E_1 E_2 E_3 E_4

E_i

Fig. Canonical ensembles with the states $(E_1, E_2, \ldots)$. $E_{tot} = E_1 + E_2 + \ldots = $ constant. M_1 ensembles for the energy E_1, M_2 ensembles for the energy E_2, and so on. In general, M_i ensembles in the energy level E_j.

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

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

where

$$\sum_j M_j = M$$

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

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

We note that the probability of finding the system in the state $|j\rangle$ is simply given by

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

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

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

Using the Stirling's formula

$$\ln W = M(\ln M - 1) - \sum_j M_j (\ln M_j - 1)$$

$$= M \ln M - \sum_j M_j \ln M_j$$

in the limit of large M and M_j. Then we have

$$\frac{1}{M}\ln W = \ln M - \frac{1}{M}\sum_j M_j \ln M_j$$

$$= \ln M - \frac{1}{M}\sum_j MP(E_j)\ln[MP(E_j)]$$

$$= \ln M - \sum_j P(E_j)\ln[P(E_j) + \ln M]$$

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

which is subject to the conditions

$$\sum_j P(E_j) = 1, \qquad \sum_j E_j P(E_j) = \langle E \rangle$$

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

$$\delta[\sum_j P(E_j)\ln P(E_j) + \alpha P(E_j) + \beta E_j P(E_j)$$

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

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

$$\beta = 1/k_{\mathrm{B}}T.$$

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

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

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

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

10. 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

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

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

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

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 $n = 0, \pm1, \pm2,\ldots$, 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.

$$H\psi_k = \frac{p^2}{2m}\psi_k = -\frac{\hbar^2}{2m}\nabla^2\psi_k = \varepsilon_k\psi_k. \tag{3}$$

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

$$\psi_k(x + L, y, z) = \psi_k(x, y, z),$$

$$\psi_k(x, y + L, z) = \psi_k(x, y, z),$$

$$\psi_k(x, y, z + L) = \psi_k(x, y, z).$$

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

$$\psi_k(r) = e^{ik\cdot r}, \tag{4}$$

with

$$k_x = (2\pi/L)\, n_x, \; (n_x = 0, \pm1, \pm2, \pm3,\ldots),$$

$$k_y = (2\pi/L)\, n_y, \; (n_y = 0, \pm1, \pm2, \pm3,\ldots),$$

$$k_z = (2\pi/L)\, n_z, \; (n_z = 0, \pm1, \pm2, \pm3,\ldots).$$

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

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

Here

$$p\psi_k(r) = \frac{\hbar}{i}\nabla_k\psi_k(r) = \hbar k\,\psi_k(r). \tag{6}$$

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

$$\left|\boldsymbol{k},\uparrow\right\rangle, \left|\boldsymbol{k},\downarrow\right\rangle.$$
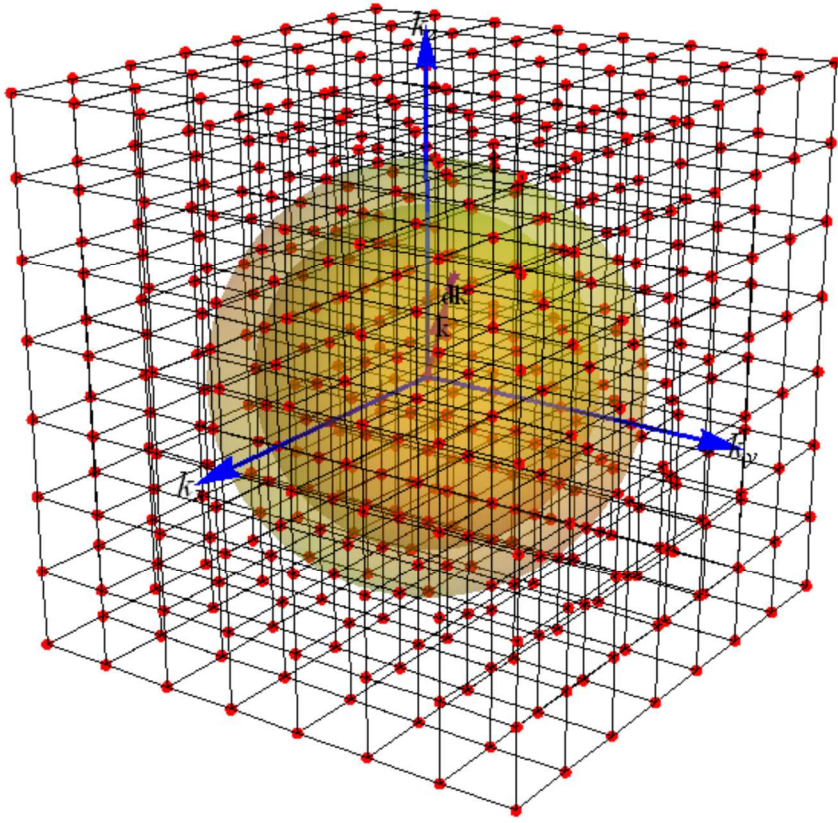

Fig.   Density of states in the 3D $\boldsymbol{k}$-space. There is one state per $(2\pi/L)^3$.

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

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

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

11.   Application of canonical ensemble for ideal gas

(a)   Partition function for the system with one atom; Z_{C1}

The partition function Z_{C1} is given by

$$Z_{C1} = \sum_k \exp(-\frac{\beta\hbar^2}{2m}k^2)$$

$$= \frac{V}{(2\pi)^3} \int d\mathbf{k} \exp(-\frac{\beta\hbar^2}{2m}k^2)$$

$$= \frac{V}{(2\pi)^3} \int 4\pi k^2 dk \exp(-\frac{\beta\hbar^2}{2m}k^2)$$

$$= \frac{V}{8\pi^2} \sqrt{\pi} C^{-3/2}$$

where $V = L^3$,

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

((Mathematica))

```
Clear["Global`*"];
f1 = V/(2 π)^3 4 π k^2 Exp[-C1 k^2];
Integrate[f1, {k, 0, ∞}] //
  Simplify[#, C1 > 0] &
```

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

Then the partition function Z_{C1} can be rewritten as

$$Z_{C1} = \frac{V\sqrt{\pi}}{8\pi^2\left(\frac{\hbar^2}{2mk_B T}\right)^{3/2}} = \frac{V}{\left(\frac{2\pi\hbar^2}{mk_B T}\right)^{3/2}} = V\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} = n_Q V$$

where n_Q is a quantum concentration and is defined by

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

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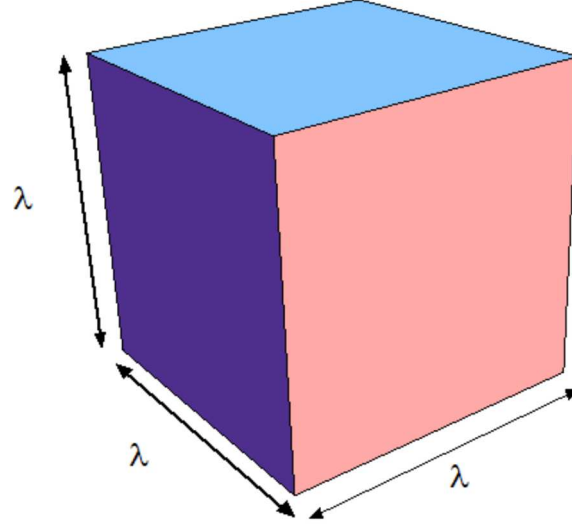

Fig.   Definition of quantum concentration. The de Broglie wavelength is on the order of interatomic distance.

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

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

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

$$\frac{1}{2}m\langle v \rangle^2 = \frac{3}{2}k_BT, \qquad \text{or} \qquad \langle v \rangle = \sqrt{\frac{3k_BT}{m}},$$

Then we have

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

where

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

It follows that

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

((Definition))

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

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

((Example))
^{4}He 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 ^{4}He 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
```

$$6.64216 \times 10^{-24}$$

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

$$7.81219 \times 10^{24}$$

```
       P1
n1 = ────── /. rule1
      kB T1
```

$$2.44631 \times 10^{19}$$

(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

$$\ln Z_N = N \ln(n_Q V) - \ln N!$$
$$= N[\ln(n_Q V) + 1 - \ln N]$$

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

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

since

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

The entropy S is obtained as

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

where

$$
\sigma_0 = \frac{5}{2} + \frac{3}{2} \ln(\frac{m k_B}{2\pi\hbar^2})
$$

Note that S can be rewritten as

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

((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

$$E = F + ST$$
$$= -Nk_BT\ln(\frac{n_Q}{n}) - Nk_BT + Nk_BT\ln\frac{n_Q}{n} + \frac{5}{2}Nk_BT$$
$$= \frac{3}{2}Nk_BT$$

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

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

leading to the Boyle's law. Then PV is

$$PV = Nk_BT = \frac{2E}{3} \qquad\qquad \text{(Bernoulli's equation)}$$

(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**))

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

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

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

The isentropic process is described by

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

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

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

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

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

12. 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

$$\begin{aligned}
Z_C &= \sum_{\alpha} \exp(-\beta E_{\alpha}) = \\
&= \int dE\, W(E) \exp(-\beta E) \\
&= \int dE \exp[\ln W(E)] \exp(-\beta E) \\
&= \int dE \exp[\ln W(E) - \beta E] \\
&= \int \exp[-N\beta f] dE
\end{aligned}$$

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

$$f(E) = \frac{\beta E - \ln W(E)}{N\beta} = \frac{1}{N}[E - Tk_B \ln W(E)]$$

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

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

where

$$\frac{\partial f(E)}{\partial E} = \frac{1}{N}[1 - k_B T \frac{\partial \ln W(E)}{\partial E}] = 0 \qquad \text{at } E = E^*$$

or

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

At $E = E^*$,

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

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

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

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

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

13. 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

$$U = \sum_\alpha p_\alpha E_\alpha$$

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

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

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

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

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

The entropy S is obtained as

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

We note that

$$-k_B \sum_\alpha p_\alpha \ln p_\alpha = -k_B \sum_\alpha p_\alpha (-\ln Z - \beta \varepsilon_\alpha)$$

$$= k_B (\beta E + \ln Z)$$

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

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

$$= S$$

Thus it follows that the entropy S is given by

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

14. Thermal average of energy fluctuation

$$U = \langle E \rangle$$

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

$$\frac{d}{dT}\langle E \rangle = \frac{d\beta}{dT}\frac{d}{d\beta}\langle E \rangle$$

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

$$= -\frac{1}{k_B T^2}\frac{d}{d\beta}[\frac{1}{Z}\sum_\alpha E_\alpha e^{-\beta E_\alpha}]$$

$$= -\frac{1}{k_B T^2}\frac{1}{Z^2}[Z\sum_\alpha(-E_\alpha^2)e^{-\beta E_\alpha} - \frac{dZ}{d\beta}\sum_\alpha E_\alpha e^{-\beta E_\alpha}]$$

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

where

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

Then we have

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

Since $\frac{d}{dT}U = C_V$, we get the relation

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

15.　　Example: ^{4}He atom as ideal gas

We consider the ^{4}He atom with mass

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

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

$$n = 2.44631 \times 1019/\text{cm}^3$$

The number of atoms in the volume $V = 10^3$ cm^3 is

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

The internal energy

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

The entropy S

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

((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 = kB N1/V1 T1 /. rule1

1.01325 × 10⁶
```

```
P1 / bar /. rule1
```

1.01325

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

1.51987×10^9

```
E1 / J /. rule1
```

151.987

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

5.12503×10^7

```
S1 / J /. rule1
```

5.12503

16.   Link
Entropy (Wikipedia)
http://en.wikipedia.org/wiki/Entropy_(statistical_thermodynamics)

REFERENCES
M. Toda, R. Kubo, and N. Saito, *Statistical Physics I: Equilibrium Statistical* (Springer, 1983).
L.D. Landau and E.M. Lifshitz, *Statistical Physics* (Pergamon Press, 1980).
R.P. Feynman, *Statistical Mechanics A Set of Lectures* (The Benjamin/Cummings, 1982).
E. Fermi, *Thermodynamics* (Dover, 1956).
S.J. Blundell and K.M. Blundel, *Concepts in Thermal Physics* (Oxford, 2006).
C. Kittel and H. Kroemer, *Thermal Physics* (W.H. Freeman and Company (1980).
C. Kittel, *Elementary Statistical Physics* (Wiley & Sons, 1958).
P. Atkins, The Laws of Thermodynamics: A Very Short Introduction (Oxford, 2010).
D.V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000).
R. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1965).
F. Bloch, *Fundamentals of Statistical Mechanics* (World Scientific, 2000).

D. ter Haar, *Elements of Statistical Mechanics* (Butterworth Heinemann, 1995).
F. Schwabl, *Statistical Mechanics*, 2nd edition (Springer, 2006).
J.W. Halley, Statistical Mechanics (Cambridge, 2007).
H. Kawamura, *Statistical Physics* (Maruzen, 1997) [in Japanese]
D. Yoshioka, Statistical Physics, An Introduction (Springer, 2007).

APPENDIX

Partition   Zustandssumme

In the classical mechanics, the partition function Z is given by

$$Z(N,V,T) = \frac{1}{h^{3N}} \int d^N \Gamma \exp[-\frac{H(^N\Gamma)}{k_B T}] \qquad \text{(phase integral)}$$

where $H(^N\Gamma)$ is the Hamiltonian in the phase space.

Laplace transformation

$$Z(N,V,T) = \sum_i e^{-\beta E_i} = \sum_E W(N,V,E) e^{-\beta E} = \int_0^\infty W(N,V,E) e^{-\beta E} dE$$

Thus the partition function is the Laplace transform of the density of states $W(N,V,E)$

Separation of Z;

   Suppose the energy of the system is a sum of subsystems which are independent to each other

$$E_i = E_i^{(1)} + E_i^{(2)} + E_i^{(3)}$$

The partition function is obtained as the product of each Z

$$Z = Z^{(1)} Z^{(2)} Z^{(3)}$$

where

$$Z^{(1)} = \sum_i e^{-\beta E_i^{(1)}} , \qquad Z^{(2)} = \sum_i e^{-\beta E_i^{(2)}} , \qquad Z^{(3)} = \sum_i e^{-\beta E_i^{(3)}}$$

Calculation of mean values in a canonical ensemble

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

$$\frac{\partial Z_C}{\partial \beta} = -\sum_i E_i e^{-\beta E_i}, \qquad \frac{\partial^2 Z_C}{\partial \beta^2} = \sum_i (-E_i)^2 e^{-\beta E_i} = \sum_i E_i^2 e^{-\beta E_i}$$

$$\langle E \rangle = U = \frac{1}{Z_C} \sum_i E_i e^{-\beta E_i} = -\frac{1}{Z_C} \frac{\partial Z_C}{\partial \beta} = -\frac{\partial \ln Z_C}{\partial \beta},$$

$$\langle E^2 \rangle = \frac{1}{Z_C} \sum_i E_i^2 e^{-\beta E_i} = \frac{1}{Z_C} \frac{\partial^2 Z_C}{\partial \beta^2}$$

$$
\begin{aligned}
(\Delta E)^2 &= \langle (E - \langle E \rangle)^2 \rangle \\
&= \langle E^2 \rangle - \langle E \rangle^2 \\
&= \frac{1}{Z} \frac{\partial^2 Z_C}{\partial \beta^2} - \frac{1}{Z_C^2} \left(\frac{\partial Z_C}{\partial \beta} \right)^2 \\
&= \frac{\partial^2 \ln Z_C}{\partial \beta^2}
\end{aligned}
$$

or

$$(\Delta E)^2 = -\frac{\partial}{\partial \beta} U = k_B T^2 \frac{\partial}{\partial T} U = k_B T^2 C$$

where C is the heat capacity.

Similarly we have

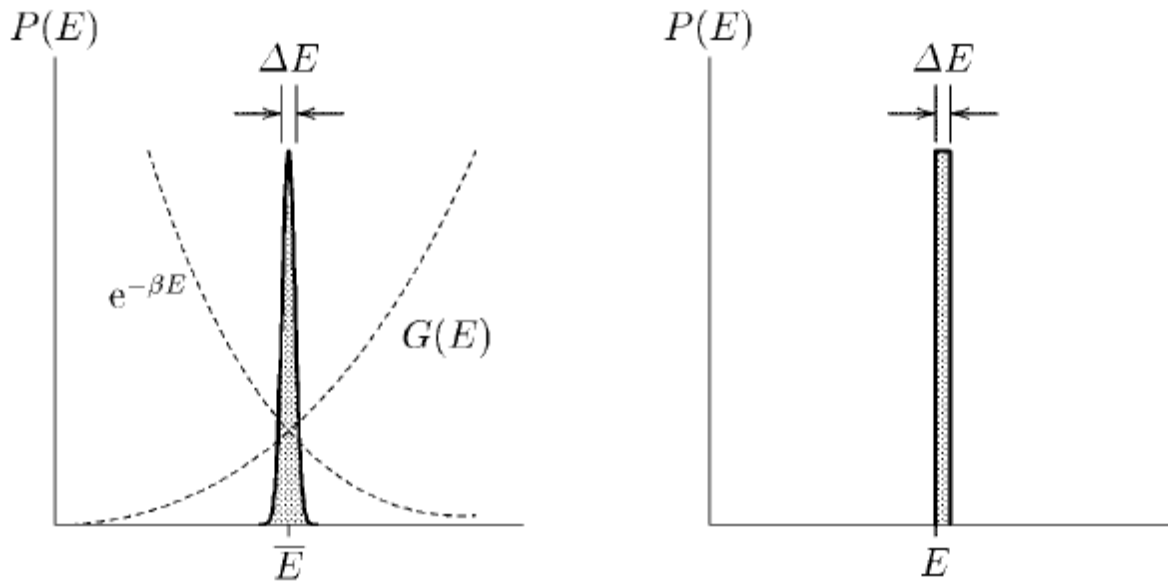$$(\Delta E)^n = (-1)^n \frac{\partial^n \ln Z_C}{\partial \beta^n}$$

Since $(\Delta E)^2$ can never be negative, it follows that $\dfrac{\partial}{\partial \beta}\langle E \rangle \le 0$ (or equivalently, that

$\dfrac{\partial}{\partial T}\langle E \rangle \ge 0$).

$$(\Delta E)^2 = k_B T^2 C \propto N, \qquad \langle E \rangle \propto N$$

$$\frac{\Delta E}{\langle E \rangle} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}$$

In the limit of $N \to \infty$ (thermodynamic limit), the energy fluctuation becomes zero.

((Adiabatic approximation))

Derivation of entropy

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

$$p_i = \frac{1}{Z_C} e^{-\beta E_i}, \qquad \sum_i p_i = 1$$

The entropy S is defined by

$$S = -k_B \sum_p p_i \ln p_i$$

$$= -k_B \sum_p p_i (-\beta E_i - \ln Z_C) \ln p_i$$

$$= k_B \beta \langle E \rangle + k_B \ln Z_C$$

$$= \frac{1}{T} \langle E \rangle + k_B \ln Z_C$$

where

$$U = \frac{1}{Z_C} \sum_i E_i e^{-\beta E_i} = -\frac{1}{Z_C} \frac{\partial Z_C}{\partial \beta} = -\frac{\partial \ln Z_C}{\partial \beta}$$

We define the Helmholtz free energy

$$F = U - ST = -k_B T \ln Z_C$$