## Method of Lagrange multiplier for the canonical ensemble Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: September 25, 2017)

Here we consider a gaseous system of N non-interacting, indistinguishable particles. The total energy E and the total number of particles are fixed. Here we derive the canonical distribution by using the method of Lagrange multiplier.



Number of ensemble



Fig. The grouping of single-particle energy levels. We assume that each energy eigenstate is non degenerate for simplicity.  $n_i$  is the number of particles in the energy level  $\varepsilon_i$ .

We consider a system of N identical particles. The energy level of one particle is given by the energy level  $\varepsilon_i$  (i = 1, 2, 3, 4...;). For simplicity we assume that each energy eigenstate is non-degenerate. Note that the discussion is almost the same even if the energy eigenstate is degenerate. The number of ways to put  $n_i$  particles in the energy level  $\varepsilon_i$  (i = 1, 2, 3, 4...;) is given by

$$W = \frac{N!}{n_1! n_2! n_3! \cdots}$$

The logarithm of *W* is given by

$$\ln W = \ln N! - \sum_{i} \ln n_{i}!$$
  

$$\approx N \ln N - N - \sum_{i} (n_{i} \ln n_{i} - n_{i})$$
  

$$= N \ln N - \sum_{i} n_{i} \ln n_{i}$$

where we use the Stirling's approximation. We note that the total particle number N and the total energy E are defined by

$$N = \sum_{i} n_{i}$$
 (restraint condition)  
$$E = \sum_{i} \varepsilon_{i} n_{i}$$
 (restraint condition)

We now apply the method of Lagrange multiplier to this system. For the variation  $\{\delta n_i\}$ 

$$\delta \ln W = -\sum_{i} (\delta n_i \ln n_i + \delta n_i) = 0,$$

or

$$\sum_{i} \delta n_{i} \ln n_{i} = 0 \tag{1}$$

$$\delta N = \sum_{i} \delta n_{i} = 0$$

$$\delta E = \sum_{i} \varepsilon_{i} \delta n_{i} = 0$$
(2)

The sum [Eq.(1) +  $\alpha$  Eq.(2) +  $\beta$  Eq.(3)] leads to an equation for the variation  $\{\delta n_i\}$ 

$$\sum_{i} (\ln n_i + \alpha + \beta \varepsilon_i) \delta n_i = 0$$

For arbitrariness of  $\delta n_i$ , we must have (for all *i*)

$$\ln n_i + \alpha + \beta \varepsilon_i = 0$$

or

$$n_i = e^{-\alpha - \beta \varepsilon_i}$$

The constants  $\alpha$  and  $\beta$  should be determined from the accessory conditions,

$$N = \sum_{i} n_{i} = \sum_{i} e^{-\alpha - \beta \varepsilon_{i}} = e^{-\alpha} \sum_{i} e^{-\beta \varepsilon_{i}}$$
$$E = \sum_{i} \varepsilon_{i} e^{-\alpha - \beta \varepsilon_{i}} = e^{-\alpha} \sum_{i} \varepsilon_{i} e^{-\beta \varepsilon_{i}}$$

The probability can be expressed by

$$P_{i} = \frac{n_{i}}{N}$$
$$= \frac{n_{i}}{\sum_{i} n_{i}}$$
$$= \frac{e^{-\alpha - \beta \varepsilon_{i}}}{e^{-\alpha} \sum_{i} e^{-\beta \varepsilon_{i}}}$$
$$= \frac{e^{-\beta \varepsilon_{i}}}{\sum_{i} e^{-\beta \varepsilon_{i}}}$$

The entropy is given by the definition

$$S = k_B \ln W$$
  
=  $k_B [N \ln N - \sum_i n_i \ln n_i]$ 

Since  $n_i = NP_i$ 

$$\frac{S}{Nk_B} = \ln N - \sum_i (P_i) \ln(NP_i)$$
$$= \ln N - \sum_i P_i (\ln N + \ln P_i)$$
$$= -\sum_i P_i \ln P_i$$

or

$$S = -Nk_B \sum_i P_i \ln P_i$$

which is a typical expression for the entropy using the probability. The constants  $\alpha$  and  $\beta$  are related to the physical properties of the system. We start with

$$\ln n_i + \alpha + \beta \varepsilon_i = 0$$

leading to

$$\sum_{i} n_i (\ln n_i + \alpha + \beta \varepsilon_i) = 0$$

or

$$\sum_{i} n_{i} \ln n_{i} = -\sum_{i} n_{i} (\alpha + \beta \varepsilon_{i}) = -\alpha N - \beta U$$

Using the entropy, this equation S can be rewritten as

$$\sum_{i} n_i \ln n_i = \frac{-S + k_B N \ln N}{k_B}$$

Then we have

$$\frac{S}{k_B} = \alpha N + \beta U + N \ln N$$

or

$$S = \alpha k_B N + k_B \beta U + k_B N \ln N \tag{1}$$

From the definition of dS, we get

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \left(\frac{\partial S}{\partial U}\right)_{V}dU + \left(\frac{\partial S}{\partial V}\right)_{U}dV$$

or

$$\left(\frac{\partial S}{\partial U}\right)_{V} = \frac{1}{T}$$
<sup>(2)</sup>

since S is a function of U and V. From Eq.(1),

$$\left(\frac{\partial S}{\partial U}\right)_{V} = k_{B}\beta \tag{3}$$

it follows that

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

The constant  $\alpha$  can be obtained as follows.

$$N = e^{-\alpha} \sum_{i} e^{-\beta \varepsilon_{i}} = e^{-\alpha} Z$$

where Z is the partition function

$$Z = \sum_{i} e^{-\beta \varepsilon_i}$$

Thus we have

$$e^{\alpha} = \frac{Z}{N}$$

and

$$P_i = \frac{1}{Z} e^{-\beta \varepsilon_i}$$
 (Maxwell-Boltzmann distribution function)

## 2. The partition function for the degenerate case

We discuss the partition function when the energy eigenstates are degenerate. We consider the partition function for the case when the energy levels 1 and 3 are non-degenerate, but the energy level 2 is degenerate with the g-degeneracy.



**Fig.** One-particle energy level. The energy eigenstate  $\varepsilon_1$  and  $\varepsilon_3$  are non-degenerate, while the energy eigenstate  $\varepsilon_2$  is g-degenerate.



Fig. Configuration of occupation states.

Then the partition function is obtained as

$$Z_{N} = \sum_{\substack{\{n_{1}, n_{21, \dots, n_{2g}}, \\ n_{3}\}}} \frac{(n_{1} + n_{21} + n_{22} + \dots + n_{2g} + n_{3})!}{n_{1}!(n_{21}!n_{22}!\cdots n_{2g}!)n_{3}!} \exp(-n_{1}\beta\varepsilon_{1} - n_{21}\beta\varepsilon_{21} - n_{22}\beta\varepsilon_{22} - \dots - \beta n_{2g}\varepsilon_{2g} - \beta n_{3}\varepsilon_{3})$$
$$= \{\exp(-\beta\varepsilon_{1}) + \sum_{j=1}^{g} \exp(-\beta\varepsilon_{2j}) + \exp(-\beta\varepsilon_{2})\}^{N}$$
$$= Z_{1}^{N}$$

where

$$\begin{split} n_1 + n_{21} + n_{22} + \ldots + n_{2g} + n_3 &= N \; . \\ \varepsilon_{21} &= \varepsilon_{22} = \ldots = \varepsilon_{2g} = \varepsilon_2 \end{split}$$

The one-particle partition function  $Z_1$  is

$$Z_1 = \exp(-\beta\varepsilon_1) + \sum_{j=1}^g \exp(-\beta\varepsilon_{2j}) + \exp(-\beta\varepsilon_2)$$
$$= \exp(-\beta\varepsilon_1) + g\exp(-\beta\varepsilon_2) + \exp(-\beta\varepsilon_2)$$

since  $\varepsilon_{21} = \varepsilon_{22} = ... = \varepsilon_{2g} = \varepsilon_2$ .

In general,  $Z_1$  can be expressed by

$$Z_1 = \sum_i g_i \exp(-\beta \varepsilon_i)$$

where  $g_i$  is the degeneracy for the energy level  $\mathcal{E}_i$ .

REFERENCES

E. Schrödinger, Statistical Thermodynamics (Cambridge, 1948).

A. Carter, Classical and Statistical Thermodynamics (Prentice Hall, 2001).

R.K. Pathria and P.D. Beale, Statistical Mechanics, third edition (Elsevier, 2011).