3. Lattice vibration

1 Boltzman distribution

1.1 Outline of Boltzman distribution

Boltzman distribution is the probability distribution or probability measure that gives the probability that a system will be in a certain state as a function of the energy of that state and the temperature of the system. The distribution is expressed in the billows,

$$n_i = \frac{N}{\sum_j exp\left(-\frac{\varepsilon_i}{k_B T}\right)} exp\left(-\frac{\varepsilon_i}{k_B T}\right) \propto exp\left(-\frac{\varepsilon_i}{k_B T}\right) \tag{1.1}$$

where, n_i is the probability of the system being in state i, N is the fixed large number of particles, ε_i is the energy of that state, k_B is Boltzman's constant (1.380×10^{-23} J/K), and T is temperature. In this chapter, the background knowledge for the derivation of boltzman distribution is presented and then the derivation is performed.

1.2 Fundamental concept of statistical mechanins

Entropy S is defined follows as Boltzmann's entropy formula,

$$S \equiv k_B \ln W \tag{2.1}$$

where the principle of equal a priori probabilities holds and the state with the largest entropy S appears most probably when it has the largest number of configurations W.

And the Temperature T is defined by using entropy S and internal energy E as follows.

$$1/T = \left(\frac{\partial S}{\partial E}\right)_{other\ conditions} \tag{2.2}$$

The above equation means that the rate of entropy increasing with increasing energy.

1.3 Lagrange multiplier

Lagrange multiplier is a strategy for finding local maxima and minima of a function subject to equality constrains. The method can be summarized Lagrangian function as follows,

$$L(x,y) = f(x,y) - \lambda g(x,y) \tag{3.1}$$

In order to find a point (a,b) where the maximum or minimum of a function $f(x,y)$ subducted to the equality constraint $g(x,y) = 0$. Where λ is called Lagrange multiplier. If at least one of $\frac{\partial g}{\partial x}$ and $\frac{\partial g}{\partial y}$ is not zero at point (a, b), then there exists λ and the following holds at point (a, b, λ).

$$\frac{\partial L(a,b)}{\partial x} = \frac{\partial L(a,b)}{\partial y} = \frac{\partial L(a,b)}{\partial \lambda} = 0 \tag{3.2}$$

On the other hand, the point (a,b) is different from points where $f(x,y)$ has maxima and minima without the constraint $g(x,y) = 0$, the following hold.

$$\frac{\partial f}{\partial x} \neq 0 \text{ and } \frac{\partial f}{\partial y} \neq 0 \tag{3.3}$$

$$\frac{\partial L}{\partial x} = 0, \frac{\partial L}{\partial y} = 0 \tag{3.4}$$

Therefore,

$$\frac{\partial f}{\partial x} = \lambda \frac{\partial g}{\partial x}, \frac{\partial f}{\partial y} = \lambda \frac{\partial g}{\partial y} \tag{3.5}$$

Thus,

$$\left(\frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}\right) = \lambda \left(\frac{\partial g}{\partial x}, \frac{\partial g}{\partial y}\right) \tag{3.6}$$

We can visualize contours of f given by $f(x, y) = d$ for various values of d, and the contour of g given by $g(x, y) = c$. The equation (3.6) means that $f = d_1$ $g = 0$ corves are parallel in the x-y plane. When (x, y) moves along $g = 0$, f does not change at a minimum/maximum (a,b). In other words, $f = d_1$ and $g = 0$ are parallel at (a,b) (fig.1). The ratio of the change of $f(x, y)$ to the change of $g(x, y)$ by changing parameters (x, y), where $f(x, y)$ and $g(x, y)$ are not constant.

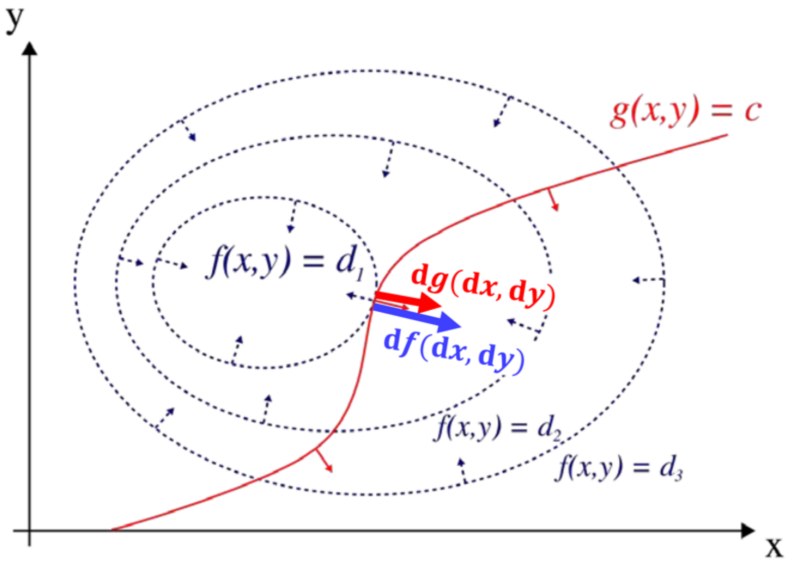

Fig. 1. The red curve shows the constraint $g(x, y) = c$. The blue curves are contours of $f(x, y)$. The point where the red constraint tangentially touches a blue contour is the maximum of $f(x, y)$ along the constraint, since $d_1 > d_2$.

1.4 Derivation of Boltzmann distribution

Considering a system composed of the fixed number of N particles with a fixed total energy E, energy of a particle is ε_i, and the number of particles having an energy ε_i is n_i. Then the total number of particles N and the total energy of the system E can be expressed as follows.

$$N = \sum_{i=0}^{\infty} n_i \tag{4.1}$$

$$E = \sum_{i=0}^{\infty} n_i \varepsilon_i \tag{4.2}$$

And here, the number of configuration of the system (n_1, n_2, n_3, …), W and the entropy of the system are as billows.

$$W = \frac{N!}{n_0!\,n_1!\,n_2!\dots} \tag{4.3}$$

$$S = k_B \ln W = k_B \ln \frac{N!}{n_0!\,n_1!\,n_2!\dots}$$
$$= k_B\,(\ln N! - \textstyle\sum_{\mathrm{i}=0} n_\mathrm{i}!) \tag{4.4}$$

Here, the Stirling's approximation is as follows.

$$\ln N! \cong N \ln N - N \tag{4.5}$$

Using the Stirling's approximation (4,5), $\ln W$ in (4.4) becomes as billows,

$$\begin{aligned} \ln W &\cong N\ln N - N - \textstyle\sum_{\mathrm{i}=0}^{\infty} n_\mathrm{i} \ln n_\mathrm{i} - n_\mathrm{i} \\ &= N\ln N - \textstyle\sum_{\mathrm{i}=0}^{\infty} n_\mathrm{i} \ln n_\mathrm{i} - n_\mathrm{i} \\ &\quad - [N - \textstyle\sum_{\mathrm{i}=0}^{\infty} n_\mathrm{i}] \\ &= N\ln N - \textstyle\sum_{\mathrm{i}=0}^{\infty} n_\mathrm{i} \ln n_\mathrm{i} \end{aligned} \tag{4.6}$$

Therefore, the conditions for the largest $\ln W$ will be $\mathrm{d} \ln W = 0$. And the total number of particles and the total energy of the system are fixed as billow from (4.1) and (4.2),

$$\mathrm{d}N = \textstyle\sum_{i=0}^{\infty} \mathrm{d}n_i = 0 \tag{4.7}$$

$$\mathrm{d}E = \textstyle\sum_{\mathrm{i}=0}^{\infty} n_i \mathrm{d}\varepsilon_i = 0 \tag{4.8}$$

Using (4.6), the change in the logarithmic number of microstates, $\ln W$ is as follows,

$$\begin{aligned} \mathrm{d} \ln W &= \mathrm{d}(N\ln N - \textstyle\sum_{\mathrm{i}=0}^{\infty} n_\mathrm{i} \ln n_\mathrm{i}) \\ &= (\mathrm{d}N + N\mathrm{d} \ln N) \\ &\quad - \textstyle\sum_{\mathrm{i}=0}^{\infty} (\mathrm{d}n_\mathrm{i} \ln n_\mathrm{i} + n_\mathrm{i} \mathrm{d} \ln n_\mathrm{i}) \\ &= -\textstyle\sum_{\mathrm{i}=0}^{\infty} (\mathrm{d}n_\mathrm{i} \ln n_\mathrm{i} + \frac{n_\mathrm{i} \mathrm{d}n_\mathrm{i}}{n_\mathrm{i}}) \\ &= -\textstyle\sum_{\mathrm{i}=0}^{\infty} (1 + \ln n_\mathrm{i}) \mathrm{d}n_\mathrm{i} \\ &\cong -\textstyle\sum_{\mathrm{i}=0}^{\infty} \ln n_\mathrm{i} \mathrm{d}n_\mathrm{i} \end{aligned} \tag{4.9}$$

Applying the method of Lagrange multiplier to obtain the maximum $\ln W$, which indicates the most probable state, under conditions of fixed N and E.

$$L = \ln W + \alpha N - \beta E \tag{4.10}$$

Where, α and β are Lagrange multiplier constant. Differentiating both sides of (4.10), we obtain

$$\begin{aligned} \mathrm{d}L &= \mathrm{d} \ln W + \alpha \mathrm{d}N - \beta \mathrm{d}E \\ &= -\textstyle\sum_{\mathrm{i}=0}^{\infty} \ln n_\mathrm{i} \mathrm{d}n_\mathrm{i} - \alpha \textstyle\sum_{\mathrm{i}=0}^{\infty} \mathrm{d}n_\mathrm{i} \\ &\quad - \beta \textstyle\sum_{\mathrm{i}=0}^{\infty} \varepsilon_i \mathrm{d}n_\mathrm{i} \end{aligned} \tag{4.11}$$

here, using (4.7) (4.8) (4.9), (4.11) becomes as billows,

$$\mathrm{d}L = -\textstyle\sum_{\mathrm{i}=0}^{\infty} (\ln n_\mathrm{i} + \alpha + \beta \varepsilon_i) \mathrm{d}n_\mathrm{i} \tag{4.12}$$

Therefore,

$$\mathrm{d}L = \textstyle\sum_{\mathrm{i}=0}^{\infty} (\ln n_\mathrm{i} + \alpha + \beta \varepsilon_i) \mathrm{d}n_\mathrm{i} = 0 \tag{4.13}$$

Thus, we obtain the following.

$$\ln n_{\mathrm{i}} + \alpha + \beta\varepsilon_i = 0 \tag{4.14}$$

From (4.14), the Boltzmann distribution (3.1) becomes as follows,

$$\begin{aligned} n_{\mathrm{i}} &= \exp(-\alpha - \beta\varepsilon_i) = \exp(-\alpha)\exp(-\beta\varepsilon_i) \\ &= A\exp(-\beta\varepsilon_i) \end{aligned} \tag{4.15}$$

Where, A is $\exp(-\alpha)$. And n_{i} and ε_i are balanced to maximize W at constant N and E. From here, determine β from (4.14). Multiplying both sides of (4.14) by $\sum_{\mathrm{i}} n_{\mathrm{i}}$, we obtain,

$$\textstyle\sum_{\mathrm{i}} n_{\mathrm{i}} \ln n_{\mathrm{i}} + \alpha \sum_{\mathrm{i}} n_{\mathrm{i}} + \beta \sum_{\mathrm{i}} n_{\mathrm{i}} = 0 \tag{4.16}$$

Using (4.6), (4.16) is changed as follow.

$$N\ln N - \ln W + \alpha\textstyle\sum_{\mathrm{i}} n_{\mathrm{i}} + \beta\sum_{\mathrm{i}=0}^{\infty} n_{\mathrm{i}}\varepsilon_i = 0 \tag{4.17}$$

By multiplying by k_B, (4.16) becomes as follow.

$$\begin{aligned} &k_B N\ln N - k_B\ln W + k_B\alpha\textstyle\sum_{\mathrm{i}} n_{\mathrm{i}} + k_B\beta\sum_{\mathrm{i}=0}^{\infty} n_{\mathrm{i}}\varepsilon_i \\ &= 0 \end{aligned} \tag{4.18}$$

From the definition of entropy (3.2), (4.18) becomes as follow.

$$k_B N\ln N - S + \alpha k_B N + \beta k_B E = 0 \tag{4.19}$$

Thus,

$$S = k_B N\ln N + \alpha k_B N + \beta k_B E \tag{4.20}$$

Differentiating (4.20) by E,

$$\frac{\mathrm{d}S}{\mathrm{d}E} = \frac{\mathrm{d}}{\mathrm{d}E}(k_B N\ln N + \alpha k_B N + \beta k_B E) = \beta k_B \tag{4.21}$$

From the definition of the temperature, T, $\frac{\mathrm{d}S}{\mathrm{d}E} = \frac{1}{T}$

$$\beta k_B = \frac{1}{T} \tag{4.22}$$

Thus,

$$\beta = \frac{1}{k_B T} \tag{4.23}$$

From here, determine the factor A of (4.15). By substituting (4.23) into (4.14),

$$\ln n_{\mathrm{i}} + \alpha + \frac{\varepsilon_i}{k_B T} = 0 \tag{4.24}$$

$$n_{\mathrm{i}} = \exp(-\alpha)\exp(-\frac{\varepsilon_i}{k_B T}) = A\exp(-\frac{\varepsilon_i}{k_B T}) \tag{4.25}$$

By substituting (4.25) into (4.1),

$$N = \textstyle\sum_{\mathrm{i}} A\exp(-\frac{\varepsilon_i}{k_B T}) \tag{4.26}$$

Thus, A is as billows.

$$\mathrm{A} = \frac{N}{\sum_{\mathrm{i}} \exp(-\frac{\varepsilon_i}{k_B T})} \tag{4.27}$$

Thus, the Boltzmann distribution can be expressed as follows (3.1).

$$n_i = \frac{N}{\sum_j exp\left(-\frac{\varepsilon_i}{k_B T}\right)} exp\left(-\frac{\varepsilon_i}{k_B T}\right) \propto exp\left(-\frac{\varepsilon_i}{k_B T}\right) \tag{1.1}$$