A Note on Statistical Mechanics

Yoshiaki Horiike

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Abstract

This article briefly reviews the derivation of important formulae of microcanonical and canonical ensemble.

1 Microcanonical Ensemble

The microcanonical system is an isolated system that does not exchange energy (or particle) outside of the system. Microcanonical ensemble assumes that every state with same energy E happens equally likely. Therefore, P_i^{M}, the probability[1] which a (quantum) microstate i happens, is given as a fraction of $W(E)$, the total number of microstates with energy E.

$$P_i^{\mathrm{M}} = \frac{1}{W(E)}$$

Ludwig Boltzmann defined the entropy S using this $W(E)$.

$$S(E) \coloneqq k_{\mathrm{B}} \ln W(E)$$

Here, k_{B} is the Boltzmann constant. The temperature of this system is defined as the partial differentiation of entropy S by energy E.

$$\frac{1}{T} \coloneqq \frac{\partial S(E)}{\partial E}$$

2 Canonical Ensemble

Consider a subpart of the microcanonical system. This small subsystem can exchange energy with the rest of whole system. From below of this section, "system" means this small subsystem, "bath"[2] means the total system except for the small subsystem, "total system" means a whole system consisting of the system and the bath.

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[1] This M stands for "Microcanonical".

[2] One can also say "reservoir".

Suppose that the system is in a state i with energy E_i. E^{bath}, the energy of the bath is equall to total energy E^{tot} without the system's energy.

$$E^{\mathrm{bath}} = E^{\mathrm{tot}} - E_i$$

By defining

- $W(E_i) = 1$ as the number of states[3] of the system with energy E_i,

- $W(E^{\mathrm{bath}})$ as the number of states of the bath with energy E^{bath},

- $W(E^{\mathrm{tot}})$ as the number of states of the total system with energy E^{tot},

we can calculate P_i^{C}, the probability[4] that system's state is in i with energy E_i as below.

$$
\begin{aligned}
P_i^{\mathrm{C}} &= \frac{W(E_i)W(E^{\mathrm{bath}})}{W(E^{\mathrm{tot}})} \\
&= \frac{W(E^{\mathrm{tot}} - E_i)}{W(E^{\mathrm{tot}})} \\
&= \exp\left[\frac{S(E^{\mathrm{tot}} - E_i) - S(E^{\mathrm{tot}})}{k_{\mathrm{B}}}\right]
\end{aligned}
$$

Thus, P_i^{C} depends on the bath's number of the states. We perform several approximations.

$$
\begin{aligned}
S(E^{\mathrm{tot}} - E_i) &= S(E^{\mathrm{tot}} - \langle E\rangle + \langle E\rangle - E_i) \\
&\approx S(E^{\mathrm{tot}} - \langle E\rangle) + \left.\frac{\partial S}{\partial E}\right|_{E=E^{\mathrm{tot}}-\langle E\rangle}(\langle E\rangle - E_i) \\
&\approx S(E^{\mathrm{tot}} - \langle E\rangle) + \frac{1}{T^{\mathrm{bath}}}(\langle E\rangle - E_i)
\end{aligned}
$$

We assumed

- $E^{\mathrm{tot}} - \langle E\rangle \gg \langle E\rangle - E_i$

- $\left.\frac{\partial S}{\partial E}\right|_{E=E^{\mathrm{tot}}-\langle E\rangle} \approx \left.\frac{\partial S}{\partial E}\right|_{E=E^{\mathrm{tot}}-E_i} = \frac{1}{T^{\mathrm{bath}}}$

in the process of approximations.

From the definition of the temperature of a microcanonical ensemble, $\frac{1}{T} := \frac{\partial S(E)}{\partial E}$, we can split $S(E^{\mathrm{tot}})$ into two terms[5].

$$S(E^{\mathrm{tot}}) = S(E^{\mathrm{tot}} - \langle E\rangle) + S(\langle E\rangle)$$

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[3]We ignored the situation of degeneracy but the essentials do not change.

[4]This C indicates "Canonical".

[5]We can confirm this by a simple example. Consider the two variables x and $y(x)$. If we know the relation $\frac{\partial y(x)}{\partial x} = a$ (a is constant), the two varialbes relation is $y(x) = ax + b$ (b is constant). We can write $y(x - \Delta x)$ as below.

$$y(x - \Delta x) = a(x - \Delta x) = ax - a\Delta x = y(x) - y(\Delta x)$$

Thus, $y(x) = y(x - \Delta x) - y(\Delta x)$.

Let's use those approximations in our calculation of P_i^{C}.

$$
\begin{aligned}
P_i^{\mathrm{C}} &= \exp\left[\frac{S(E^{\mathrm{tot}} - E_i) - S(E^{\mathrm{tot}})}{k_{\mathrm{B}}}\right] \\
&\approx \exp\left[\frac{S(E^{\mathrm{tot}} - \langle E \rangle) + \frac{1}{T^{\mathrm{bath}}}(\langle E \rangle - E_i) - S(E^{\mathrm{tot}} - \langle E \rangle) - S(\langle E \rangle)}{k_{\mathrm{B}}}\right] \\
&= \exp\left[\frac{\langle E \rangle - E_i - T^{\mathrm{bath}}S(\langle E \rangle)}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right] \\
&= \exp\left[\frac{\langle E \rangle - T^{\mathrm{bath}}S(\langle E \rangle)}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right]\exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right] \\
&= \exp\left[\frac{F}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right]\exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right] \\
&= \frac{1}{Z}\exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right] \\
&\propto \exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right]
\end{aligned}
$$

We defined several new quantities.

- $\langle E \rangle := \sum_i P_i^{\mathrm{C}} E_i$ is average energy of the system.

- $F := \langle E \rangle - T^{\mathrm{bath}} S(\langle E \rangle)$ is free energy.

- $Z := \exp\left[-\frac{F}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right]$ is the partition function.

From the definition of a partition function above, we can obtain free energy as a function of partition function.

$$
F := -k_{\mathrm{B}} T \ln Z
$$

From the normalization condition of probability P_i^{C}, we can derive another form of a partition function.

$$
\begin{aligned}
1 &= \sum_i P_i^{\mathrm{C}} \\
&= \sum_i \frac{1}{Z}\exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right] \\
&= \frac{1}{Z}\sum_i \exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right]
\end{aligned}
$$

Hence, we define a partition function as a normalization factor of probability.

$$
Z := \sum_i \exp\left[-\frac{E_i}{k_{\mathrm{B}}T^{\mathrm{bath}}}\right]
$$