BOLTZMANN DISTRIBUTION

Basic algorithm of statistical mechanics. Recall the fundamental postulate:

> *A system isolated for a long time flips to every one of its microstates with equal probability*.

The fundamental postulate suggests a basic algorithm of statistical mechanics:

1. Construct an isolated system with an internal variable, x.
2. Use the internal variable x to dissect the whole set of the microstates of the isolated system into subsets. When the internal variable takes value x, the isolated system flips among a subset of its microstates. Obtain the number of the microstates in this subset, $\Omega(x)$.
3. After the system is isolated for a long time, the probability for the internal variable to take value x is $\Omega(x)/\Omega_{total}$, where Ω_{total} is the total number of microstates of the isolated system.

This basic algorithm of statistical mechanics is equivalent to the fundamental postulate. We now apply this algorithm to obtain the Boltzmann distribution. We adopt the following convention:

- log means the logarithm of the natural base, so that $d\log x/dx = 1/x$.
- The Boltzmann constant is set to be k = 1, so that entropy is dimensionless, $S = \log\Omega$, and temperature has the same unit as energy, $1/T = \partial\log\Omega/\partial U$.

A system in thermal contact with a reservoir of energy. Consider a system in thermal contact with a much larger system. We will call the system the small system. We will call the larger system the reservoir of energy, or just *reservoir* for brevity. By thermal contact we mean that the two systems exchange energy, but do not exchange space, matter, or electric charge. The composite—the system and the reservoir together—is an isolated system.

Small system. The small system can be in any one of a set of microstates:

$$\{\gamma_1, \gamma_2, \ldots\}.$$

Because the small system exchanges energy with the reservoir, the microstates of the small system may have different amounts of energy. When the small system is in microstate γ_s, the energy of the microstate is U_s. We list the energies of all the microstates:

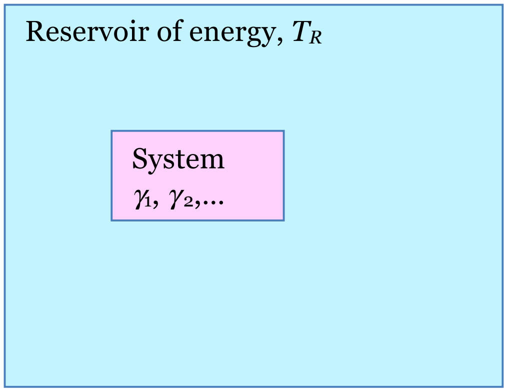
$$\{U_1, U_2, \ldots\}.$$

The list may have repetitive entries, because some different microstates may have the same energy.

The small system is not isolated, and flips to different microstates with different probabilities. Let P_s be the probability for the small system to be in microstate γ_s. We list the probabilities of all the microstates:

$$\{P_1, P_2, \ldots\}.$$

This list is called the *distribution of probability*. After the composite is isolated for a long time, this distribution of probability becomes time-independent, and is called the Boltzmann distribution. We next calculate this distribution of probability.



Reservoir. When the energy of the reservoir, U_R, is fixed at one value, the reservoir becomes an isolated system, and flips among a set of microstates. Let Ω_R be the number of this set of microstates. The number of microstates is a function of energy, $\Omega_R(U_R)$. This function is smooth because the reservoir is a large system.

The temperature of the reservoir, T_R, is defined by

$$\frac{\partial \log \Omega_R(U_R)}{\partial U_R} = \frac{1}{T_R}.$$

In thermal contact with the small system, the reservoir may gain or lose small amounts of energy, but the reservoir will keep its temperature fixed. Consequently, in speaking of a small system in thermal contact with a reservoir, to focus attention on the system, we often do not mention the reservoir, and simply say that the small system is held at a fixed temperature. This verbal change does not eliminate the need for the reservoir, for it is the reservoir that holds the small system at the fixed temperature. Thus, the phrase "a small system held at a temperature" is synonymous to "a small system in thermal equilibrium with a reservoir of a fixed temperature".

Construct an isolated system with an internal variable. The small system and the reservoir together constitute an isolated system. An internal variable of the isolated system is the microstate of the small system. The small system can be in any one of the microstate $\left\{\gamma_1,\gamma_2,...\right\}$. We next use this internal variable to dissect the isolated system (i.e., the composite of the small system and the reservoir).

Use the internal variable to dissect the whole set of the microstates of the isolated system. The isolated system conserves its energy. Let the total energy of the isolated system be U_{total}. When the small system is in a microstate γ_s, the energy of the small system is U_s, the energy of the reservoir is $U_{total}-U_s$, and the number of microstates of the reservoir is

$$\Omega_R\left(U_{total}-U_s\right).$$

Recall that

$$\frac{\partial\log\Omega_R\left(U_R\right)}{\partial U_R}=\frac{1}{T_R}.$$

The energy of the small system is small compared to the total energy of the isolated system, $U_s << U_{total}$. We expand the function $\log\Omega_R\left(U_{total}-U_s\right)$ into the Taylor series of U_s, namely,

$$\log\Omega_R\left(U_{total}-U_s\right)=\log\Omega_R\left(U_{total}\right)-\frac{U_s}{T_R}.$$

Here we only retain up to the term linear in U_s.

Take exponential of both sides of the above equation, and we obtain that

$$\Omega_R\left(U_{total}-U_s\right)=\Omega_R\left(U_{total}\right)\exp\left(-\frac{U_s}{T_R}\right).$$

When isolated at energy U_{total}, the number of microstates of the reservoir is $\Omega_R\left(U_{total}\right)$. Upon losing energy U_s and being isolated at energy $U_{total}-U_s$, the reservoir reduces its number of microstates by a factor $\exp\left(-U_s/T_R\right)$. This factor is called the *Boltzmann factor*.

Calculate the distribution of probability. A microstate of the isolated system is specified by a microstate of the small system and a microstate of the reservoir. Let us count the total number of microstates of the isolated system, Ω_{total}. When the small system is in a particular microstate γ_s, the reservoir flips among a set of microstates, and the number of such microstates is $\Omega_R\left(U_{total}-U_s\right)$. Consequently, the total number of microstates of the isolated system is

$$\Omega_{total}=\sum\Omega_R\left(U_{total}-U_s\right)=\Omega_R\left(U_{total}\right)\sum\exp\left(-\frac{U_s}{T_R}\right).$$

The sum is over all microstates of the small system:

$$Z=\sum\exp\left(-\frac{U_s}{T_R}\right).$$

This sum of the Boltzmann factors is called the *partition function*. The partition function is a function of the temperature of the reservoir, $Z\left(T_R\right)$.

Recall the fundamental postulate: a system isolated for a long time flips to every one of its microstates with equal probability. That is, the isolated system is equally probable in each of the set of Ω_{total} microstates. A subset of the microstates of the isolated system is when the small system is in the microstate γ_s and the reservoir is in any one of the $\Omega_R\left(U_{total}-U_s\right)$ number of microstates. Consequently, the probability for the small system to be in the microstate γ_s is

$$P_s=\frac{\Omega_R\left(U_{total}-U_s\right)}{\Omega_{total}},$$

namely,

$$P_s=\frac{1}{Z}\exp\left(-\frac{U_s}{T_R}\right).$$

This distribution of probability is called the *Boltzmann distribution*.

After the small system and the reserve together are isolated for a long time, they equilibrate. The probability for the small system to be in a microstate γ_s depends on the energies of the microstates of the system, $U_1,U_2,...$, and on the temperature of the reservoir, T_R. This probability is independent of any other characteristics of the small system and the reservoir. In particular, this probability does not require us to ask the question, what is the temperature of the small system? This question is meaningless when the small system is small, and the number of microstates of the small system is a discrete function of the energy of the small system.

Mean energy of the small system. In thermal equilibrium with the reservoir, the small system fluctuates among its microstates $\left\{\gamma_1,\gamma_2,...\right\}$. The mean energy of the small system is

$$\langle U\rangle = \sum P_s U_s .$$

The sum is over all the microstates of the small system.

Inserting the expressions for the probability, we obtain that

$$\langle U\rangle = \sum \frac{U_s}{Z}\exp\left(\frac{-U_s}{T_R}\right).$$

Recalling the expression of the partition function, we can confirm that

$$\langle U\rangle = T_R^2 \frac{d\log Z\left(T_R\right)}{dT_R} .$$

This equation gives the mean energy of the small system in terms of the partition function $Z\left(T_R\right)$.

Entropy of a system in thermal equilibrium with a reservoir. The following expression defines the *entropy of a distribution of probability*.

$$S = -\sum P_s \log P_s .$$

See the supplement for a justification of this definition.

Inserting the Boltzmann distribution into the above expression, we obtain that

$$S = -\sum \frac{1}{Z}\exp\left(-\frac{U_s}{T_R}\right)\log\left[\frac{1}{Z}\exp\left(-\frac{U_s}{T_R}\right)\right].$$

A direct calculation gives that

$$S = \log Z + T_R \frac{d\log Z\left(T_R\right)}{dT_R} .$$

This equation gives the mean entropy of the small system in terms of the partition function $Z\left(T_R\right)$.

Helmholtz function of a system in thermal equilibrium with a reservoir. We have previously defined the Helmholtz function as

$$F = U - T_R S .$$

Now interpret U and S by the mean energy and entropy. We obtain that

$$F = -T_R \log Z .$$

This equation relates the Helmholtz function to the microstates of the system.

Invert the above relation, and we obtain that

$$Z = \exp\left(-\frac{F}{T_R}\right).$$

Write the Boltzmann distribution as

$$P_s = \exp\left(\frac{F - U_s}{T_R}\right).$$

Supplement: Entropy of a Distribution of Probability

A sample space of outcomes of unequal probability. Consider a sample space—that is, the set of all possible outcomes of an experiment:

$$\left\{\gamma_1, \gamma_2, ...\right\}$$

The distribution of probability is

$$\left\{P_1, P_2, ...\right\}.$$

Each probability is nonnegative, and

$$P_1 + P_2 + ... = 1.$$

The sum is over all sample points. In general, the probabilities are unequal.

A definition of entropy of a distribution of probability. Define the *entropy* S of the distribution of probability by

$$S = -P_1 \log P_1 - P_2 \log P_2 - ...$$

The sum is over all sample points. As a convention we will use the logarithm of the natural base. Because $x \log x \to 0$ as $x \to 0$, we set $0 \log 0 = 0$. Because $0 \le P(\gamma_i) \le 1$, the number $-\log P(\gamma_i)$ is nonnegative.

A heuristic justification for the definition. Imagine a large number n copies of the system. Write

$$n_i = nP_i.$$

Because $P_1 + P_2 + ... = 1$, we have

$$n_1 + n_2 + ... = n.$$

The sum is over all sample points.

The n copies of the system constitute a giant system. Specify a state of the giant system by placing n_s copies of the system in state γ_s. The number of states of the giant system is

$$\Omega_{giant} = \frac{n!}{n_1! n_2! ...}.$$

The giant system flips to each of its state with equal probability, $1/\Omega_{giant}$. Recall the definition of entropy of a system of equal probability of all microstates. The entropy of the giant system is

$$S_{giant} = \log \Omega_{giant}.$$

Stirling's Approximation. The approximation is derived by approximating $\log n!$, for a large n, with an integral:

$$\begin{aligned}\log n! &= \log 1 + \log 2 + \ldots + \log n \\ &\approx \int_1^n \log x\, dx \\ &= \left(x \log x - x\right)\Big|_1^n \\ &= n \log - n + 1 \\ &\approx n \log - n\end{aligned}$$

Using this approximation, we obtain that

$$S_{giant} = -n_1 \log \frac{n_1}{n} - n_2 \log \frac{n_2}{n} - \ldots$$

The mean entropy per copy of the system is

$$S = \frac{S_{giant}}{n}.$$

The mean entropy per copy of the system is

$$S = -\sum P_s \log P_s .$$

This expression defines the *entropy of a distribution of probability*.

A sample space of outcomes of equal probability. We have defined the entropy for sample space of a general distribution of probability. We now specialize the definition for a sample space of an equal distribution of probability. Consider a sample space of Ω outcomes:

$$\gamma_1, \gamma_2, \ldots, \gamma_\Omega .$$

Every outcome is equally probable. Thus, the probability of each event is

$$P_s = 1/\Omega .$$

The entropy is

$$S = -\Omega(1/\Omega)\log(1/\Omega) = \log \Omega .$$

This equation recovers the familiar definition of entropy.

Entropy in the theory of probability. To calculate the entropy, all we need is a distribution of probability. No more, no less. The physical nature of the experiment is irrelevant, be it tossing a coin, rolling a die, or drinking a glass of wine.

We do not introduce entropy by following the accidents in the history of thermodynamics. Entropy is a mathematical concept independent of the concept of energy and temperature. The entropy of rolling a die is just as valid a concept as the entropy of a glass of wine. Entropy is a number calculated from a distribution of probability.

The situation is like integrating a function. An integral is a number calculated from a function. You may integrate a function in engineering, or a function in economics. There is no difference between an engineer's integration and an economist's integration. The difference is in the applications, not in the integration.