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The Canonical Ensemble

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1. The Canonical Ensemble

We will develop the method of canonical ensembles by considering a system placed in a heat bath at temperature T. The canonical ensemble is the assembly of systems with fixed N and V. In other words we will consider an assembly of systems closed to others by rigid, diathermal, impermeable walls. The energy of the microstates can fluctuate, the system is kept in equilibrium by being in contact with the heat bath at temperature T. Schematically, we can view this ensemble as:

State 1 $\boxed{E_1, V, N}$ Bath T

State 2 $\boxed{E_2, V, N}$ Bath T

State 3 $\boxed{E_3, V, N}$ Bath T

$\vdots$

State ν $\boxed{E_\nu, V, N}$ Bath T

The system for which the canonical ensemble is appropriate can be thought of as a sub-system of the system for which the microcanonical ensemble is appropriate.
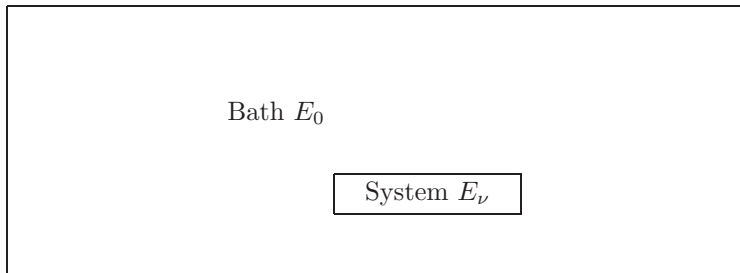
Bath E_0

System E_ν

Isolated system with E, V, N fixed.

Basically what we do is to examine one state and consider the rest to be in the heat bath. Thus the macroscopic system is specified by

$T, V,$ and$N$ as illustrated.
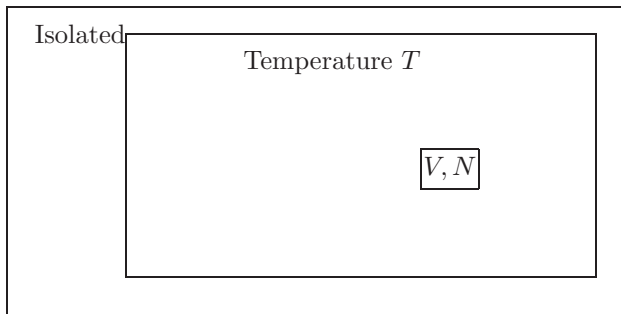
Let the combined energy of the system and the heat bath $= E_0$

The system with V, N will be in one of a variety of microstates $E_1, E_2, \ldots, E_r$. These energies could be degenerate in some cases, but

we assume that they can be ordered.

$$E_1 \leq E_2 \leq E_3 \leq \ldots \leq E_r \leq \ldots$$

We'll select δE so that we select one energy level but several microstates.

Let the system be in a state with energy E_r, the energy of the reservoir is then $E_0 - E_r$.

What's the probability that the system will be in a microstate with energy E_r? When we considered an isolated system, we found the probability of it being in a macrostate specified by (E, V, N, α) was proportional to the multiplicity $\Omega(E, V, N, \alpha)$. In this situation, we could choose to analyze the system or the heat bath. It will prove to be efficient to analyze the heat bath.

The multiplicity of the heat bath is:

$$\Omega(E_0 - E_r)$$

We have an isolated system with two sub-systems, labelling the heat bath as system 2, we have:

$$p_r = \text{const}\Omega_2(E_0 - E_r)$$

The ratio of probabilities for the states E_i, and E_j is

$$\frac{p_i}{p_j} = \frac{\Omega_2(E_0 - E_i)}{\Omega_2(E_0 - E_j)}$$

We could write similar expressions for all pairs of levels, if we consider three

$$\frac{p_i}{p_i} = \frac{\Omega_2(E_0 - E_i)}{\Omega_2(E_0 - E_i)}$$

$$\frac{p_i}{p_j} = \frac{\Omega_2(E_0 - E_i)}{\Omega_2(E_0 - E_j)}$$

$$\frac{p_i}{p_k} = \frac{\Omega_2(E_0 - E_i)}{\Omega_2(E_0 - E_k)}$$

we can add them to give

$$\frac{p_i + p_j + p_k}{p_i} = \frac{\Omega_2(E_0 - E_i) + \Omega_2(E_0 - E_j + \Omega_2(E_0 - E_k))}{\Omega_2(E_0 - E_i)}$$

We can generalize this result to yield

$$p_r = \frac{\Omega_2(E_0 - E_r)}{\sum\limits_i \Omega_2(E_0 - E_i)}$$

Where the sum is taken over all levels. Next, we rewrite the expression for p_r in terms of the reservoir entropy.

$S = k \ln \Omega$, so $S/k = \ln \Omega$, and $\Omega = e^{S/k}$. Using this we write

$$p_r = (\text{constant}) \times \exp\left(\frac{S_2(E_0 - E_r)}{k}\right)$$

With a large reservoir, we can assume that $E_0 \gg E_r$. If the heat bath is large this inequality holds for all states with a reasonable chance of occurring. Now we'll expand in a Taylor series about $S_2(E_0)$. Recall

$$f(x_0 + a) = f(x_o) + a \left(\frac{df}{dx} \right)_{x=x_0} + \frac{1}{2!} a^2 \left(\frac{d^2 f}{dx^2} \right)_{x=x_0} + \dots$$

so

$$\frac{1}{k} S_2(E_0 - E_r) = \frac{1}{k} S_2(E_0) - \frac{E_r}{k} \frac{\partial S_2(E_0)}{\partial E_0} + \frac{E_r^2}{2!k} \frac{\partial^2 S_2(E_0)}{\partial E_0^2} \dots$$

Now, we know that

$$\frac{\partial S_2(E_0)}{\partial E} = \frac{1}{T}$$

where T is the temperature of the heat bath. Thus, we have

$$\frac{1}{k} S_2(E_0 - E_r) = \frac{1}{k} S_2(E_0) - \frac{E_r}{kT}.$$

All higher order partial derivatives are zero by assumption of a large heat bath

$$\frac{\partial^2 S_2}{\partial E^2} = \frac{\partial}{\partial E}\left(\frac{1}{T}\right) = 0$$

Now using

$$p_r = \frac{\Omega_2(E_0 - E_r)}{\sum\limits_i \Omega_2(E_0 - E_i)}$$

and

$$\Omega = e^{S/k}$$

and substituting

$$\beta = \frac{1}{kT}$$

we get

$$p_r = \frac{exp(\frac{S_2}{k} - \beta E_r)}{\sum\limits_i exp(\frac{S_2}{k} - \beta E_i)}$$

$$= \frac{e^{S_2/k}e^{-\beta E_r}}{\sum_i e^{S_2/k}e^{-\beta E_i}}$$

$$= \frac{e^{-\beta E_r}}{\sum_i e^{-\beta E_i}}$$

$$p_r = \frac{e^{-\beta E_r}}{Z}$$

2. Partition Functions and the Boltzmann Distribution

In the last equation, I have defined

$$Z = \sum_i e^{-\beta E_i} = \text{Sum over States} = \text{Zustandsumme} = \text{Partition Function}$$

We will also use an alternate definition where the sum is over energy levels rather than states. In this alternate definition, we let the

degeneracy of the level be $g(E_i)$. Then

$$Z = \sum_{E_i} g(E_i) e^{-\beta E_i}.$$

The equation $p_r = \frac{e^{-\beta E_r}}{Z}$ is called the Boltzmann distribution. The Boltzmann distribution gives the probability that is in a particular state when it is in a heat bath at temperature T. Z plays a central rôle in the study of systems at fixed T. The term $e^{-\beta E_r}$ is called the Boltzmann factor.

It is now time to combine these ideas with our knowledge of probability, recall

$$<x> = \sum_i x_i f(x_i) = \sum_i p_i x_i$$

In thermal physics, in the canonical ensemble, the probability distribution ($p_i = f(x_i)$ is the Boltzmann distribution, the average is called an ensemble average.

2.1. Average Energy in the Canonical Ensemble

$$<E> = \sum_i p_i E_r = \frac{1}{Z} \sum_r E_r e^{-\beta E_r}$$

Let's simplify this result, consider $Z = \sum_r e^{-\beta E_r}$

$$
\begin{aligned}
\frac{\partial Z}{\partial \beta} &= \frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r} \\
&= \sum_r e^{-\beta E_r} \frac{\partial}{\partial \beta}(-\beta E_r) \\
&= -\sum_r E_r e^{-\beta E_r}
\end{aligned}
$$

so

$$<E> = \frac{1}{Z} \sum_r E_r e^{-\beta E_r}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_r e^{-\beta E_r}$$

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

$$<E> = -\frac{\partial\ln Z}{\partial\beta}$$

This is an average over the states of the system that exchange energy with the reservoir. The fluctuations around this energy are small.

3. Gibbs Entropy Formula

Consider a general macroscopic system with state labelled $1, 2, 3, \ldots, r, \ldots$. The probability that a system is in a state r is p_r. Without constraints, $\sum p_r = 1$ is all about the way we can say about the system. The general definition of entropy is then

$$S = -k\sum_r p_r \ln p_r.$$

This is the Gibbs entropy formula. We can deduce this formula for a generalized ensemble. Consider an ensemble of ν replicas of our system. We'll assume that each replica has the same probability $p_2, p_2, p_3, \ldots, p_r, \ldots$ of being in the state i. Provided ν is large enough, the number or systems in the ensemble in state r is

$$\nu_r = \nu p_r$$

The multiplicity Ω_ν for the ensemble with ν_1 subsystems in state 1, ν_2 subsystems in state 2, etc., is the number of ways the distribution can be realized:

$$\Omega_\nu = \frac{\nu!}{\nu_1! \nu_2! \ldots \nu_r!}$$

Now

$$S_\nu = k \ln \Omega_\nu = k \ln \frac{\nu!}{\nu_1! \nu_2! \ldots \nu_r!}$$

$$S_\nu = k \ln \nu! - k(\ln \nu_1! + \nu_2! + \ldots + \nu_r!)$$

Recall Stirling's approximation $\ln N! = N \ln N - N$, so

$$S_\nu = k(\nu \ln \nu - \sum_r \nu_r \ln \nu_r)$$

But $\nu_r = \nu p_r$

$$
\begin{aligned}
S_\nu &= k\nu \ln \nu - k \sum_r \nu p_r \ln(\nu p_r) \\
&= k\nu \ln \nu - k\nu \sum_r p_r \ln(\nu p_r) \\
&= k\nu \ln \nu - k\nu \sum_r p_r \ln \nu - k\nu \sum_r p_r \ln p_r \\
&= k\nu \ln \nu - k\nu \ln \nu \sum_r p_r - k\nu \sum_r p_r \ln p_r \\
S_\nu &= -k \ln \nu \sum_r p_r \ln p_r
\end{aligned}
$$

But entropy is extensive so the entropy of one system (replica) is

$$S = S_\nu = -k \sum_r p_r \ln p_r$$

The Gibbs entropy formula is consistent with the Boltzmann entropy formula $S = k \ln \Omega$. In an isolated system with energy in the range E to $E + \delta E$, the number of microstates in the interval is $\Omega(E, V, N)$. The probability of finding the system in one of the microstates is $1/\Omega(E, V, N)$ in the range and 0 outside the range. So

$$p_r = \frac{1}{\Omega(E, V, N)} \qquad \text{(there are } \Omega \text{ terms in an isolated system)}$$

$$S = -k \sum_r p_r \ln p_r = -k \sum_r p_r \ln \frac{1}{\Omega} = k \ln \Omega \sum_r p_r = k \ln \Omega$$

4. Entropy of a System in a Heat Bath

To find the entropy of a system in a heat bath, we can use the Gibbs entropy formula and the Boltzmann distribution for p_r.

$$S = -k \sum_r p_r \ln p_r$$

and

$$p_r = \frac{e^{-\beta E_r}}{Z}.$$

Combining these expressions, and simplifying

$$
\begin{aligned}
-\frac{S}{k} &= \sum_r p_r \ln p_r \\
&= \sum_r \frac{e^{-\beta E_r}}{Z} \ln \left(\frac{e^{-\beta E_r}}{Z} \right) \\
&= \sum_r \frac{e^{-\beta E_r}}{Z} \ln \left(e^{-\beta E_r} \right) - \sum_r \frac{e^{-\beta E_r}}{Z} \ln Z
\end{aligned}
$$

$$= \sum_r \frac{e^{-\beta E_r}}{Z} \left(-\beta E_r\right) - \frac{Z}{Z} \ln Z$$

$$= \sum_r \frac{-\beta E_r e^{-\beta E_r}}{Z} - \ln Z$$

but, by definition, we have

$$<E> = \sum_r \frac{E_r e^{-\beta E_r}}{Z},$$

so we can simplify the above result to yield

$$-\frac{S}{k} = -\beta <E> - \ln Z,$$

and finally we find

$$S = \frac{<E>}{T} + k \ln Z.$$

We will usually assume that the system energy is well defined and use $<E>$ and E interchangeably, that is the system's mean energy

(which is an estimate) and the system's energy are interchangeable.
Our development of the partition function through its ensemble tells
us that $Z = Z(T, V, N)$, thus S and $<E>$ are also functions of
T, V, and N.

5. Summary

$$S = -k \sum_r p_r \ln p_r$$

$$p_r = \frac{e^{-\beta E_r}}{Z}$$

$$Z = \sum_r e^{-\beta E_r}$$

$$<E> = \frac{1}{Z} \sum_r E_r e^{-\beta E_r}$$

$$<E> = -\frac{\partial \ln Z}{\partial \beta}$$

$$S = \frac{<E>}{T} + k \ln Z = S(T, V, N)$$

In these expressions, Z and $<E>$, and as a consequence S are defined as functions of T, V, and N. Contrast this with an isolated system where $S = S(T, V, N)$. For a macroscopic system at temperature T, energy fluctuations are negligible — i.e. to $<E>$. This means that the entropy of a macroscopic body is a heat bath at temperature T is well defined and is equal to that of an isolated body with energy E equal to the mean energy $<E>$ of the system at temperature T. We can express this as

$$S(T, V, N) = k \ln \Omega(<E>, V, N)$$

For an isolate system, the basic quantities are Ω and S; for a system in a heat bath, the basic quantities are $Z(T, V, N)$ and $F(T, V, N)$. We have defined enthalpy, a function useful for studying isolated systems at fixed pressure. F is a similar thermodynamic quantity, defined as

$F = E - TS$, useful for analyzing systems in equilibrium with a heat bath at temperature T, that is systems held at constant temperature. We will now relate this function to the partition function.

6. Helmholtz Free Energy, F

If we define $F = E - TS$, and note that for a macroscopic system $E = <E>$, we can write

$$F = E - TS = -kT \ln Z(T, V, N),$$

and use

$$S = \frac{<E>}{T} + k \ln Z$$

resulting in

$$F(T, V, N) = <E> - TS = -kT \ln Z.$$

This concludes the basic development of the partition function and the canonical ensemble, we will later explore other theoretical developments, it is now time to look at some examples.