Chapter 6

Entropy

Our introduction to the concept of entropy will be based on the canonical distribution,
\[ \rho(H) = \frac{e^{-\beta H}}{Z}. \]  

(6.1)

Classically, we can define the mean volume of phase space occupied by
\[ \rho(\bar{E}) \Delta q \Delta p = 1, \]  

(6.2)

where \( \bar{E} = \langle H \rangle \) is the average energy. Then, we define the entropy by
\[ S = k \ln \Delta q \Delta p = -k \ln \rho(\bar{E}). \]  

(6.3)

For the canonical distribution, \( \ln \rho(H) = \text{const} - \beta H \), so
\[ \ln \rho(\bar{E}) = \langle \ln \rho(H) \rangle = \int dq \, dp \, \rho \ln \rho. \]  

(6.4)

Thus the entropy is
\[ S = -k \langle \ln \rho \rangle = -k \int dq \, dp \, \rho \ln \rho. \]  

(6.5)

Quantum mechanically, we define the number of quantum states by
\[ \rho(\bar{E}) \Delta \Gamma = 1, \]  

(6.6)

and then the entropy is
\[ S = k \ln \Delta \Gamma = -k \ln \rho(\bar{E}) = -k \langle \ln \rho \rangle = -k \text{Tr} \rho \ln \rho. \]  

(6.7)

Note that because
\[ \rho(H) = \sum_n \lvert n \rangle p_n \langle n \rvert, \]  

(6.8)
where the sum is over a complete set of states, the entropy can also be written as
\[ S = -k \sum_n p_n \ln p_n \geq 0, \] (6.9)
because \( 1 \geq p_n \geq 0 \), so the entropy is zero only for a pure state. For the canonical distribution, this occurs only at \( T = 0 \). The correspondence principle relation between the number of quantum states and the volume of phase space is
\[ \Delta \Gamma = \frac{\Delta q \Delta p}{h^s}, \] (6.10)
for \( s \) degrees of freedom, where \( h = 2\pi \hbar \) is Planck’s constant.
If we have two independent systems, so that
\[ \rho = \rho_1 \rho_2, \quad \text{Tr} \rho_1 = \text{Tr} \rho_2 = 1, \] (6.11)
the entropy of the composite system is
\[ S = -k [\text{Tr} (\rho_1 \ln \rho_1) \text{Tr} \rho_2 + \text{Tr} (\rho_2 \ln \rho_2) \text{Tr} \rho_1] \]
\[ = -k (\text{Tr} \rho_1 \ln \rho_1 + \text{Tr} \rho_2 \ln \rho_2) \]
\[ = S_1 + S_2, \] (6.12)
that is, entropies are additive.

The entropy is closely related to the quantity \( P \) introduced in Chapter 2, the number of ways of getting a distribution \( \{a_l\} \):
\[ P = \frac{N!}{\prod_l (a_l)!}, \] (6.13)
where the ensemble consists of \( N \) systems, and \( a_l \) is the number of systems in the \( l \)th state, so
\[ N = \sum_l a_l. \] (6.14)
What we actually maximized was \( \ln P \), which is
\[ \ln P = \ln N! - \sum_l \ln (a_l)! \approx N \ln N - \sum_l a_l \ln a_l, \] (6.15)
which uses Stirling’s approximation and Eq. (6.14). The probability of finding a system in the \( l \)th state is \( p_l = a_l/N \), so
\[ \ln P = N \ln N - N \sum_l p_l (\ln p_l + \ln N) = -N \sum_l p_l \ln p_l, \] (6.16)
This is the content of the third law of thermodynamics, which states that if the ground state is non-degenerate, the entropy vanishes at absolute zero.
or
\[ \frac{k}{N} \ln P = S; \]  \hspace{1cm} (6.17)

\( k \ln P \) is actually the entropy of the entire ensemble. So we see that of all distributions, with fixed \( N \) and \( E \), the most probable distribution, the canonical distribution, maximizes the entropy.

Now, let us see what \( S \) is more explicitly in the canonical distribution, for which
\[ p_n = \frac{e^{-\beta E_n}}{Z}, \quad Z = \sum_n e^{-\beta E_n}. \]  \hspace{1cm} (6.18)

Then the entropy is
\[ S = -k \text{Tr} \rho \ln \rho = -k \sum_n p_n \ln p_n \]
\[ = -k \sum_n \frac{e^{-\beta E_n}}{Z} \left[ -\beta E_n - \ln Z \right] \]
\[ = k\beta U + k \ln Z. \]  \hspace{1cm} (6.19)

We have two kinds of energy appearing here: The internal energy,
\[ U = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z} \sum_n E_n e^{-\beta E_n}, \]  \hspace{1cm} (6.20)

and the Helmholtz free energy,
\[ F = -kT \ln Z, \quad T = \frac{1}{k\beta}. \]  \hspace{1cm} (6.21)

The relation (6.19) says that these are related by
\[ F = U - TS, \]  \hspace{1cm} (6.22)

which should be familiar from thermodynamics. If I take the differential of \( \ln Z \),
\[ d \ln Z = d\beta \frac{d}{d\beta} \ln Z + \sum_l \frac{dE_l}{d\beta} \ln Z \]
\[ = -U d\beta - \frac{\beta}{Z} \sum_l e^{-\beta E_l} dE_l, \]  \hspace{1cm} (6.23)

which is equivalent to
\[ d(\ln Z + \beta U) = \beta (dU - \sum_l p_l dE_l), \]  \hspace{1cm} (6.24)

where by Eq. (6.19) the differential on the left is \( dS/k \). Inside the parenthesis on the right, \( dU \) represents the average internal energy increase, while \( -\sum_l p_l dE_l \) represents the average work done by the system when the energy levels are
lifted from $E_i$ to new energy levels $E_i + dE_i$. We call the latter $\delta W$, where $\delta$ is a reminder that there is no system property called work (unlike energy or entropy), and so $\delta W$ depends upon the path. Then Eq. (6.24) reads

$$dS = \frac{1}{T} \delta Q, \quad \delta Q = dU + \delta W,$$

(6.25)

where $\delta Q$ is the heat supplied to the system. That heat either does work on the system, or changes its internal energy. $1/T$ is the integrating factor necessary to change the imperfect differential $\delta Q$ into the perfect differential $dS$. This, in fact, is the rigorous thermodynamic definition of temperature.

Note that thermodynamic relations, such as

$$dF = dU - TdS - SdT = -pdV + TdS - TdT = -pdV - SdT,$$

(6.26)

or

$$\left( \frac{\partial F}{\partial T} \right)_V = -S, \quad \left( \frac{\partial F}{\partial V} \right)_T = -p,$$

(6.27)

may also be derived statistically,

$$\left( \frac{\partial F}{\partial T} \right)_V = -k \ln Z + kT \frac{1}{Z} \sum_l \left( -\frac{E_l}{kT^2} \right) e^{-\beta E_l},$$

$$= \frac{F - U}{T} = -S,$$

(6.28)

because the energy levels don’t change if the volume is fixed, and

$$\left( \frac{\partial F}{\partial V} \right)_T = -kT \frac{1}{Z} \sum_l \left( -\beta \right) \frac{\partial E_l}{\partial V} e^{-\beta E_l},$$

$$= -\frac{\delta W}{\delta V} = -p.$$

(6.29)

Finally, let us rederive the thermodynamic relation, used above,

$$dU = -pdV + TdS.$$

(6.30)

This says

$$\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T}.$$

(6.31)

In fact, from

$$S = k\beta U + k \ln Z,$$

(6.32)

we see

$$\left( \frac{\partial S}{\partial U} \right)_V = k\beta + kU \left( \frac{\partial \beta}{\partial U} \right)_V + k \left( \frac{\partial}{\partial U} \ln Z \right)_V$$

$$= k\beta = \frac{1}{T},$$

(6.33)
where the last two terms on the first line cancel because
\[
\frac{\partial}{\partial U} \ln Z = \frac{\partial}{\partial \beta} \ln Z \frac{\partial \beta}{\partial U} = -U \frac{\partial \beta}{\partial U},
\] (6.34)
provided the volume is held fixed, which means that the energy levels \(E_l\) do not change.

6.1 Examples

6.1.1 Ideal Gas
Recall that for an ideal gas [Eq. (5.44)]
\[
Z = V^N \left(\frac{2\pi m \beta}{\bar{\hbar}^2}\right)^{3N/2}.
\] (6.35)
Then the free energy is
\[
F = -kT \ln Z = -kT \left(N \ln V + \frac{3N}{2} \ln T + \text{constant}\right).
\] (6.36)
The internal energy is
\[
U = \frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} \frac{1}{\beta} = \frac{3N}{2} kT,
\] (6.37)
which is the equipartition theorem. The pressure is given by the ideal gas law:
\[
p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NkT}{V}, \quad pV = NkT.
\] (6.38)

6.1.2 Harmonic Oscillator
In this case, the energy levels are
\[
E_l = \left(l + \frac{1}{2}\right) \bar{\hbar} \omega, \quad l = 0, 1, 2, \ldots.
\] (6.39)
Then the partition function is
\[
Z = \sum_l e^{-\beta E_l} = e^{-\beta \bar{\hbar} \omega / 2} \sum_{l=0}^{\infty} e^{-\beta \bar{\hbar} \omega} = e^{-\beta \bar{\hbar} \omega / 2} \frac{1}{1 - e^{-\beta \bar{\hbar} \omega}} = \frac{1}{e^{\beta \bar{\hbar} \omega / 2} - e^{-\beta \bar{\hbar} \omega / 2}} = \frac{1}{2 \sinh \beta \bar{\hbar} \omega / 2}.
\] (6.40)
Then the free energy is

\[ F = -kT \ln Z = kT \ln \sinh \frac{\beta \hbar \omega}{2} + kT \ln 2. \] (6.41)

The internal energy is

\[
U = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{\sinh \beta \hbar \omega/2} \cosh \beta \hbar \omega/2 \left( \frac{\hbar \omega}{2} \right) = \frac{\hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2} \\
= \frac{\hbar \omega}{2} e^{\beta \hbar \omega/2} + e^{\beta \hbar \omega/2} = \frac{\hbar \omega}{2} e^{\beta \hbar \omega} + 1 \\
= \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}, \] (6.42)

which is the famous Planck distribution. Note the appearance in the first term of the zero-point energy.

### 6.1.3 Two-level System

Here the system has only two states of energy

\[ E = 0 \quad \text{and} \quad E = \epsilon. \] (6.43)

This is sometimes called a Fermi oscillator. The partition function is

\[ Z = 1 + e^{-\beta \epsilon}, \] (6.44)

and so the free energy is

\[ F = -kT \ln \left( 1 + e^{-\beta \epsilon} \right), \] (6.45)

from which we find the internal energy

\[
U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{1}{1 + e^{-\beta \epsilon}}(-\epsilon)e^{-\beta \epsilon} = \frac{\epsilon}{e^{\beta \epsilon} + 1}, \] (6.46)

which is the famous Fermi distribution.

### 6.2 Fluctuations

Let us consider the spread in energies about the average,

\[ \langle (H - U)^2 \rangle = \langle H^2 \rangle - U^2. \] (6.47)

Now the internal energy is

\[ U = -\frac{d}{d \beta} \ln Z = \frac{1}{Z} \frac{d}{d \beta} Z, \] (6.48)
6.2. FLUCTUATIONS

so

\[ U^2 = \left( \frac{1}{Z} \frac{d}{d\beta} Z \right)^2, \] (6.49)

while

\[ \langle H^2 \rangle = \sum_l p_l E_l^2 = \frac{1}{Z} \sum_l e^{-\beta E_l} E_l^2 = \frac{1}{Z} \frac{d^2}{d\beta^2} Z, \] (6.50)

so

\[ \langle (H - U)^2 \rangle = \frac{1}{Z} \frac{d^2}{d\beta^2} Z - \left( \frac{1}{Z} \frac{d}{d\beta} Z \right)^2 = \frac{d^2}{d\beta^2} \ln Z. \] (6.51)

On the other hand, the specific heat at constant volume is defined by

\[ c_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{d\beta}{dT} \frac{dU}{d\beta} = \frac{1}{kT^2} \frac{d^2}{d\beta^2} \ln Z \]

\[ = \frac{1}{kT^2} \langle (H - U)^2 \rangle. \] (6.52)

Thus we define the root mean square fluctuation in the energy as

\[ \delta E = \sqrt{\langle (H - U)^2 \rangle}, \] (6.53)

we have

\[ \delta E = \sqrt{c_V T}. \] (6.54)

If the specific heat is independent of \( T \), the fluctuation in the energy grows linearly with the temperature. For an ideal gas,

\[ U = \frac{3N}{2} kT, \] (6.55)

so \( c_V = 3Nk/2 \), and

\[ \delta E = \sqrt{\frac{3N}{2} kT}, \quad \frac{\delta E}{U} = \sqrt{\frac{2}{3N}}, \] (6.56)

which exhibits the typical \( 1/\sqrt{N} \) behavior of statistical fluctuations.