

Chapter 6

Entropy

Our introduction to the concept of entropy will be based on the canonical distribution,

$$\rho(H) = \frac{e^{-\beta H}}{Z}. \quad (6.1)$$

Classically, we can define the mean volume of phase space occupied by

$$\rho(\bar{E}) \Delta q \Delta p = 1, \quad (6.2)$$

where $\bar{E} = \langle H \rangle$ is the average energy. Then, we define the entropy by

$$S = k \ln \Delta q \Delta p = -k \ln \rho(\bar{E}). \quad (6.3)$$

For the canonical distribution, $\ln \rho(H) = \text{const} - \beta H$, so

$$\ln \rho(\bar{E}) = \langle \ln \rho(H) \rangle = \int dq dp \rho \ln \rho. \quad (6.4)$$

Thus the entropy is

$$S = -k \langle \ln \rho \rangle = -k \int dq dp \rho \ln \rho. \quad (6.5)$$

Quantum mechanically, we define the number of quantum states by

$$\rho(\bar{E}) \Delta \Gamma = 1, \quad (6.6)$$

and then the entropy is

$$S = k \ln \Delta \Gamma = -k \ln \rho(\bar{E}) = -k \langle \ln \rho \rangle = -k \text{Tr } \rho \ln \rho. \quad (6.7)$$

Note that because

$$\rho(H) = \sum_n |n\rangle p_n \langle n|, \quad (6.8)$$

where the sum is over a complete set of states, the entropy can also be written as

$$S = -k \sum_n p_n \ln p_n \geq 0, \quad (6.9)$$

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 $T = 0$.¹ The correspondence principle relation between the number of quantum states and the volume of phase space is

$$\Delta\Gamma = \frac{\Delta q \Delta p}{h^s}, \quad (6.10)$$

for s degrees of freedom, where $h = 2\pi\hbar$ is Planck's constant.

If we have two independent systems, so that

$$\rho = \rho_1 \rho_2, \quad \text{Tr } \rho_1 = \text{Tr } \rho_2 = 1, \quad (6.11)$$

the entropy of the composite system is

$$\begin{aligned} S &= -k \text{Tr } \rho_1 \rho_2 (\ln \rho_1 + \ln \rho_2) \\ &= -k [\text{Tr } (\rho_1 \ln \rho_1) \text{Tr } \rho_2 + \text{Tr } (\rho_2 \ln \rho_2) \text{Tr } \rho_1] \\ &= -k (\text{Tr } \rho_1 \ln \rho_1 + \text{Tr } \rho_2 \ln \rho_2) \\ &= S_1 + S_2, \end{aligned} \quad (6.12)$$

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 $\{a_l\}$:

$$P = \frac{N!}{\prod_l (a_l)!}, \quad (6.13)$$

where the ensemble consists of N systems, and a_l is the number of systems in the l th state, so

$$N = \sum_l a_l. \quad (6.14)$$

What we actually maximized was $\ln P$, which is

$$\ln P = \ln N! - \sum_l \ln(a_l)! \approx N \ln N - \sum_l a_l \ln a_l, \quad (6.15)$$

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

$$\ln P = N \ln N - N \sum_l p_l (\ln p_l + \ln N) = -N \sum_l p_l \ln p_l, \quad (6.16)$$

¹This 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

$$\frac{k}{N} \ln P = S; \quad (6.17)$$

$k \ln P$ 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

$$p_n = \frac{e^{-\beta E_n}}{Z}, \quad Z = \sum_n e^{-\beta E_n}. \quad (6.18)$$

Then the entropy is

$$\begin{aligned} S &= -k \text{Tr } \rho \ln \rho = -k \sum_n p_n \ln p_n \\ &= -k \sum_n \frac{e^{-\beta E_n}}{Z} [-\beta E_n - \ln Z] \\ &= k\beta U + k \ln Z. \end{aligned} \quad (6.19)$$

We have two kinds of energy appearing here: The internal energy,

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z} \sum_n E_n e^{-\beta E_n}, \quad (6.20)$$

and the Helmholtz free energy,

$$F = -kT \ln Z, \quad T = \frac{1}{k\beta}. \quad (6.21)$$

The relation (6.19) says that these are related by

$$F = U - TS, \quad (6.22)$$

which should be familiar from thermodynamics. If I take the differential of $\ln Z$,

$$\begin{aligned} d \ln Z &= d\beta \frac{d}{d\beta} \ln Z + \sum_l dE_l \frac{d}{dE_l} \ln Z \\ &= -U d\beta - \frac{\beta}{Z} \sum_l e^{-\beta E_l} dE_l, \end{aligned} \quad (6.23)$$

which is equivalent to

$$d(\ln Z + \beta U) = \beta(dU - \sum_l p_l dE_l), \quad (6.24)$$

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_l to new energy levels $E_l + dE_l$. We call the latter δW , where δ is a reminder that there is no system property called work (unlike energy or entropy), and so δW depends upon the path. Then Eq. (6.24) reads

$$dS = \frac{1}{T}\delta Q, \quad \delta Q = dU + \delta W, \quad (6.25)$$

where δQ 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 δQ into the perfect differential dS . This, in fact, is the rigorous thermodynamic definition of temperature.

Note that thermodynamic relations, such as

$$\begin{aligned} dF &= dU - TdS - SdT = -pdV + TdS - TdS - SdT \\ &= -pdV - SdT, \end{aligned} \quad (6.26)$$

or

$$\left(\frac{\partial F}{\partial T}\right)_V = -S, \quad \left(\frac{\partial F}{\partial V}\right)_T = -p, \quad (6.27)$$

may also be derived statistically,

$$\begin{aligned} \left(\frac{\partial F}{\partial T}\right)_V &= -k \ln Z + kT \frac{1}{Z} \sum_l \left(-\frac{E_l}{kT^2}\right) e^{-\beta E_l} \\ &= \frac{F - U}{T} = -S, \end{aligned} \quad (6.28)$$

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

$$\begin{aligned} \left(\frac{\partial F}{\partial V}\right)_T &= -kT \frac{1}{Z} \sum_l (-\beta) \frac{\partial E_l}{\partial V} e^{-\beta E_l} \\ &= -\frac{\delta W}{dV} = -p. \end{aligned} \quad (6.29)$$

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

$$dU = -pdV + TdS. \quad (6.30)$$

This says

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}. \quad (6.31)$$

In fact, from

$$S = k\beta U + k \ln Z, \quad (6.32)$$

we see

$$\begin{aligned} \left(\frac{\partial S}{\partial U}\right)_V &= k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_V + k \left(\frac{\partial}{\partial U} \ln Z\right)_V \\ &= k\beta = \frac{1}{T}, \end{aligned} \quad (6.33)$$

where the last two terms on the first line cancel because

$$\frac{\partial}{\partial U} \ln Z = \frac{\partial}{\partial \beta} \ln Z \frac{\partial \beta}{\partial U} = -U \frac{\partial \beta}{\partial U}, \quad (6.34)$$

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)]

$$Z = V^N \left(\frac{2\pi m}{\beta} \right)^{3N/2}. \quad (6.35)$$

Then the free energy is

$$F = -kT \ln Z = -kT \left(N \ln V + \frac{3N}{2} \ln T + \text{constant} \right). \quad (6.36)$$

The internal energy is

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} \frac{1}{\beta} = \frac{3N}{2} kT, \quad (6.37)$$

which is the equipartition theorem. The pressure is given by the ideal gas law:

$$p = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{NkT}{V}, \quad pV = NkT. \quad (6.38)$$

6.1.2 Harmonic Oscillator

In this case, the energy levels are

$$E_l = \left(l + \frac{1}{2} \right) \hbar \omega, \quad l = 0, 1, 2, \dots \quad (6.39)$$

Then the partition function is

$$\begin{aligned} Z &= \sum_l e^{-\beta E_l} = e^{-\beta \hbar \omega / 2} \sum_{l=0}^{\infty} e^{-\beta l \hbar \omega} \\ &= e^{-\beta \hbar \omega / 2} \frac{1}{1 - e^{-\beta \hbar \omega}} = \frac{1}{e^{\beta \hbar \omega / 2} - e^{-\beta \hbar \omega / 2}} \\ &= \frac{1}{2 \sinh \beta \hbar \omega / 2}. \end{aligned} \quad (6.40)$$

Then the free energy is

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

The internal energy is

$$\begin{aligned} U &= -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{\sinh \beta \hbar \omega / 2} \cosh \beta \hbar \omega / 2 \left(\frac{\hbar \omega}{2} \right) = \frac{\hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2} \\ &= \frac{\hbar \omega}{2} \frac{e^{\beta \hbar \omega / 2} + e^{-\beta \hbar \omega / 2}}{e^{\beta \hbar \omega / 2} - e^{-\beta \hbar \omega / 2}} = \frac{\hbar \omega}{2} \frac{e^{\beta \hbar \omega} + 1}{e^{\beta \hbar \omega} - 1} \\ &= \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}, \end{aligned} \quad (6.42)$$

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

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

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

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

and so the free energy is

$$F = -kT \ln (1 + e^{-\beta \epsilon}), \quad (6.45)$$

from which we find the internal energy

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

which is the famous Fermi distribution.

6.2 Fluctuations

Let us consider the spread in energies about the average,

$$\langle (H - U)^2 \rangle = \langle H^2 \rangle - U^2. \quad (6.47)$$

Now the internal energy is

$$U = -\frac{d}{d\beta} \ln Z = -\frac{1}{Z} \frac{d}{d\beta} Z, \quad (6.48)$$

so

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

while

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

so

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

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

$$\begin{aligned} c_V &= \left(\frac{\partial U}{\partial T} \right)_V = \frac{d\beta}{dT} \frac{dU}{d\beta} = \frac{1}{kT^2} \frac{d^2}{d\beta^2} \ln Z \\ &= \frac{1}{kT^2} \langle (H - U)^2 \rangle. \end{aligned} \quad (6.52)$$

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

$$\delta \mathcal{E} = \sqrt{\langle (H - U)^2 \rangle}, \quad (6.53)$$

we have

$$\delta \mathcal{E} = \sqrt{k c_V T}. \quad (6.54)$$

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

$$U = \frac{3N}{2} kT, \quad (6.55)$$

so $c_V = 3Nk/2$, and

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

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