Appendix C: Entropy

In classical contexts, “entropy” is a quantitative way to describe our lack of knowledge about a system. In information theory, information entropy describes our uncertainty about the contents of a message before receiving it. In thermodynamics and statistical mechanics, thermodynamic entropy describes our uncertainty about the microscopic details (“microstate”) of a complex many-body system. In fact, these two formulations are closely related and mutually consistent; for a discussion of this relationship, see Feynman (2000). Here, we will use the statistical mechanics point of view.

Suppose a system has discrete microstates labeled by integers \( \{1, 2, 3, \ldots\} \), which have probabilities \( \{p_1, p_2, p_3, \ldots\} \). Then the entropy of the system is defined as

\[
S_{\text{cl}} = -k_B \sum_i p_i \ln(p_i).
\]

The probabilities \( p_i \) are conditional probabilities, conditioned on the known facts about the macroscopic features of the system (e.g., we might know the total energy \( E \)).

If we know exactly which microstate the system is in (i.e., \( p_k = 1 \) for some state \( k \)), the entropy formula gives \( S_{\text{cl}} = 0 \). The opposite situation, of “complete uncertainty”, is provided by a micro-canonical ensemble: a system that is at equilibrium, has a fixed total energy \( E \), and does not interact with the rest of the universe. In this case, the ergodicity postulate of statistical mechanics states that all possible microstates with energy \( E \) are equally probable. If there are \( W \) possible microstates, the probabilities are

\[
p_i = \frac{1}{W} \quad \forall i \in \{1, 2, \ldots, W\}.
\]

Therefore, the entropy formula gives

\[
S_{\text{cl}} = -k_B W \frac{1}{W} \ln(1/W) = k_B \ln W,
\]

the famous result carved into the gravestone of Ludwig Boltzmann (1844–1906). Note that this expression has an implicit energy dependence: changing \( E \) varies \( W \) and hence \( S_{\text{cl}} \).

The entropy formula is designed so that any other probability distribution, which describes a situation of partial uncertainty, yields an entropy \( S_{\text{cl}} \) lying between 0 and \( k_B \ln W \). To see that zero is the lower bound, first note that for \( 0 \leq p_i \leq 1 \), each term in the entropy formula satisfies \( -k_B p_i \ln(p_i) \geq 0 \), and the equality holds if and only if \( p_i = 0 \) or \( p_i = 1 \). See the figure below:

![Entropy Graph](image-url)
This implies that $S_{\text{cl}} \geq 0$, and moreover that $S_{\text{cl}} = 0$ if and only if $p_i = \delta_{ik}$ for some $k$ (i.e., there is no uncertainty). Next, it can be shown that $k_B \ln W$ is the upper bound (which implies the second law of thermodynamics). We will not go over the details of that proof, but it follows from a mathematical relation known as Gibbs’ inequality.

Another important feature of the entropy formula is that $S_{\text{cl}}$ is extensive, meaning that it scales (“extends”) proportionally with system size. To see this, consider two independent systems $A$ and $B$, which have microstate probabilities $\{p^A_i\}$ and $\{p^B_j\}$. If we regard the combination of $A$ and $B$ as a single system, each microstate of the combined system is specified by the microstate of $A$ and the microstate of $B$, and is thus indexed by integers $(i, j)$, with probability $p_{ij} = p^A_i p^B_j$. The entropy of the combined system is

$$S_{\text{cl}} = -k_B \sum_{ij} p^A_i p^B_j \ln (p^A_i p^B_j)$$

$$= -k_B \left( \sum_i p^A_i \ln p^A_i \right) \left( \sum_j p^B_j \ln p^B_j \right)$$

$$= S_{\text{cl}}^A + S_{\text{cl}}^B,$$

where $S_{\text{cl}}^A$ and $S_{\text{cl}}^B$ are the individual entropies of the $A$ and $B$ subsystems.

This has important consequences for the behavior of $W(E)$, the number of microstates at each energy $E$. Suppose we extend a system by adding micro-canonical subsystems (which are insulated from each other). In the process, both $E$ and $S_{\text{cl}}$ increase proportionally. Since $S_{\text{cl}} \propto \ln[W(E)],$

$$E \propto \ln W \Rightarrow W(E) \propto e^{\beta_0 E} \text{ for some } \beta_0 > 0.$$

If we relax the restriction that the additional subsystems are micro-canonical, the number of microstates grows even faster with $E$, as energy can now be distributed in different ways between the subsystems. It is reasonable to assume that the scaling is a faster-growing exponential,

$$W(E) \propto e^{\beta E} \text{ for some } \beta \geq \beta_0.$$

This implies that the constant of proportionality relating $S_{\text{cl}}$ and $E$ is

$$\frac{\partial E}{\partial S_{\text{cl}}} = \frac{1}{k_B \beta} = T,$$

where $\beta \equiv (k_B T)^{-1}$ defines the temperature $T$. This is the first law of thermodynamics.

A canonical ensemble is a system held in equilibrium with a larger system, called a “heat bath”. We can model this with a micro-canonical ensemble of energy $E$, divided into two subsystems, $A$ (the canonical ensemble) and $B$ (the heat bath), which are not insulated from each other. Using the ergodicity postulate, and the aforementioned exponential scaling of $W$ with $E$, one can show that the probability for subsystem $A$ to have energy $E_A$ is

$$p_A(E_A) \propto W_A(E_A) e^{-\beta E_A},$$

where $W_A(E_A)$ is the number of microstates of energy $E_A$ for subsystem $A$, and $\beta$ is the inverse temperature of the heat bath. This is the celebrated Boltzmann law. It implies that each microstate $i$, of energy $E_i$, has probability

$$p_i = \frac{\exp(-\beta E_i)}{Z}, \text{ where } Z \equiv \sum_j \exp(-\beta E_j).$$
$Z(\beta, E_1, E_2, \ldots)$ is called the **partition function**. Note that $p_i$ satisfies probability conservation, $\sum_i p_i = 1$, and that the sum involves all microstates of all possible energies.

The probability distribution for a canonical ensemble represents a partial-uncertainty situation, since lower-energy microstates are more probable than higher-energy microstates. Plugging the above expression for $p_i$ into the entropy formula gives:

$$S_{\text{cl}} = \frac{1}{T} \sum E_i e^{-\beta E_i} + k_B \ln Z = \frac{\langle E \rangle}{T} + k_B \ln Z,$$

where $\langle E \rangle = \sum_i E_i p_i$ denotes the average energy. We can then define

$$F \equiv -k_B T \ln Z = \langle E \rangle - T S_{\text{cl}},$$

and show that this satisfies $\partial F/\partial T = -S_{\text{cl}}$. This quantity can be identified as the thermodynamic **free energy**.

**Further Reading**