Chapter 11

Energy

In Chapter 9 of these notes we introduced the Principle of Maximum Entropy as a technique for estimating probability distributions consistent with constraints.

A simple case that can be done analytically is that in which there are three probabilities, one constraint in the form of an average value, and the fact that the probabilities add up to one. There are, then, two equations in three unknowns, and it is straightforward to express the entropy in terms of one of the unknowns, eliminate the others, and find the maximum. This approach also works if there are four probabilities and two average-value constraints, in which case there is again one fewer equation than unknown.

Another special case is one in which there are many probabilities but only one average constraint. Although the entropy cannot be expressed in terms of a single probability, the solution in Chapter 9 is practical if the summations can be calculated.

In the application of the Principle of Maximum Entropy to physical systems, the number of possible states is usually very large, so that neither analytic nor numerical solutions are practical. Even in this case, however, the Principle of Maximum Entropy is useful because it leads to relationships among different quantities. In this chapter we look at general features of such systems.

Because we are now interested in physical systems, we will express entropy in Joules per Kelvin rather than in bits, and use the natural logarithm rather than the logarithm to the base 2.

11.1 Magnetic Dipole Model

Most of the results below apply to the general multi-state model of a physical system implied by quantum mechanics; see Chapter 10. However, an important aspect is the dependence of energy on external parameters. For example, for the magnetic dipole, the external parameter is the magnetic field H. Here is a brief review of the magnetic dipole so it can be used as an example below.

This model was introduced in section 9.1.2. Figure 11.1 shows a system with two dipoles and two environments for the system to interact with. (Of course any practical system will have many more than two dipoles, but the important ideas can be illustrated with only two.) The dipoles are subjected to an externally applied magnetic field H, and therefore the energy of the system depends on the orientations of the dipoles and on the applied field. Each dipole, both in the system and in its two environments, can be either "up" or "down," so there are four possible states for the system, "up-up," "up-down," "down-up," and "down-down." The energy of a dipole is $m_d H$ if down and $-m_d H$ if up, and the energy of each of the four states is the sum of the energies of the two dipoles.
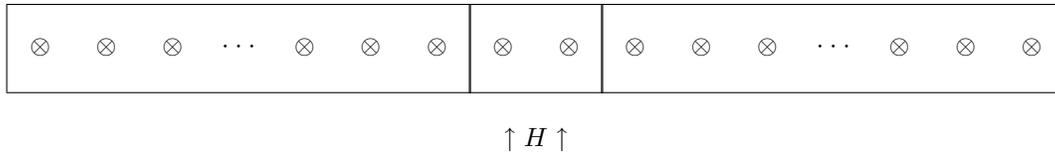

$$\uparrow H \uparrow$$

Figure 11.1: Dipole moment example. Each dipole can be either up or down

11.2 Principle of Maximum Entropy for Physical Systems

According to the multi-state model motivated by quantum mechanics (see Chapter 10 of these notes) there are a finite (or countable infinite) number of quantum states of the system. We will use i as an index over these states. The states have energy E_i, and might have other physical attributes as well. After these states are enumerated and described, the Principle of Maximum Entropy can be used, as a separate step, to estimate how likely each state is to be occupied.

We denote the occupancy of state i by the event A_i. The state i has probability $p(A_i)$ of being occupied. For simplicity we will write this probability $p(A_i)$ as p_i. We use the Principle of Maximum Entropy to estimate the probability distribution p_i consistent with the average energy E being a known (for example, measured) quantity $\widetilde{E}$. Thus

$$\widetilde{E} = \sum_i p_i E_i \tag{11.1}$$

$$1 = \sum_i p_i \tag{11.2}$$

The entropy is

$$S = k_B \sum_i p_i \ln\left(\frac{1}{p_i}\right) \tag{11.3}$$

where $k_B = 1.38 \times 10^{-23}$ Joules per Kelvin and is known as Boltzmann's constant.

The probability distribution that maximizes S subject to a constraint like Equation 11.2 was presented in Chapter 9, Equation 9.12. That formula was for the case where entropy was expressed in bits; the corresponding formula for physical systems, with entropy expressed in Joules per Kelvin, is the same except for the use of e rather than 2:

$$p_i = e^{-\alpha} e^{-\beta E_i} \tag{11.4}$$

so that

$$\ln\left(\frac{1}{p_i}\right) = \alpha + \beta E_i \tag{11.5}$$

The sum of the probabilities must be 1 and therefore

$$\alpha = \ln\left(\sum_i e^{-\beta E_i}\right) \tag{11.6}$$

As expressed in terms of the Principle of Maximum Entropy, the objective is to find the various quantities given the expected energy E. However, except in the simplest circumstances it is usually easier to do calculations the other way around. That is, it is easier to use β as an independent variable, calculate α in terms of it, and then find the p_i and then the entropy S and energy E.

11.2.1 General Properties

Because β plays a central role, it is helpful to understand intuitively how different values it may assume affect things.

First, if $\beta = 0$, all probabilities are equal. This can only happen if the number of states is finite.

Second, if $\beta > 0$, then states with lower energy have a higher probability of being occupied. Similarly, if $\beta < 0$, then states with higher energy have a higher probability of being occupied. Because of the exponential dependence on energy, unless $\mid \beta \mid$ is small, the only states with much probability of being occupied are those with energy close to the minimum possible (β positive) or maximum possible (β negative).

Third, we can multiply the equation above for $ln(1/p_i)$ by p_i and sum over i to obtain

$$S = k_B(\alpha + \beta E) \tag{11.7}$$

This equation is valid and useful even if it is not possible to find β in terms of E or to compute the many values of p_i.

Fourth, in Section 11.2.2 we will look at a small change dE in E and inquire how the other variables change. Such first-order relationships, or "differential forms," provide intuition which helps when the formulas are interpreted.

Fifth, in Section 11.2.3 we will consider the dependence of energy on an external parameter, using the magnetic dipole system with its external parameter H as an example.

The critical equations above are listed here for convenience

$$1 = \sum_i p_i \tag{11.8}$$

$$E = \sum_i p_i E_i \tag{11.9}$$

$$S = k_B \sum_i p_i \ln\left(\frac{1}{p_i}\right) \tag{11.10}$$

$$p_i = e^{-\alpha}e^{-\beta E_i} \tag{11.11}$$

$$\alpha = \ln\left(\sum_i e^{-\beta E_i}\right)$$

$$= \frac{S}{k_B} - \beta E \tag{11.12}$$

11.2.2 Differential Forms

Now suppose E_i does not depend on an external parameter, and E changes by a small amount dE. We will calculate from the equations above the changes in the other quantities, keeping only first-order variations (i.e., neglecting terms like $(dE)^2$ which, for small enough dE, are insignificantly small)

$$0 = \sum_i dp_i \tag{11.13}$$

$$dE = \sum_i E_i \, dp_i \tag{11.14}$$

$$dS = k_B \sum_i \ln\left(\frac{1}{p_i}\right) dp_i + k_B \sum_i p_i\, d\left[ln\left(\frac{1}{p_i}\right)\right]$$

$$= k_B \sum_i \ln\left(\frac{1}{p_i}\right) dp_i - k_B \sum_i \left(\frac{p_i}{p_i}\right) dp_i$$

$$= k_B \sum_i (\alpha + \beta E_i)\, dp_i$$

$$= k_B \beta\, dE \tag{11.15}$$

$$d\alpha = \left(\frac{1}{k_B}\right) dS - \beta\, dE - E\, d\beta$$

$$= -E\, d\beta \tag{11.16}$$

$$dp_i = p_i(-d\alpha - E_i\, d\beta)$$

$$= -p_i(E_i - E)\, d\beta \tag{11.17}$$

from which it is not difficult to show

$$dE = -\left(\sum_i p_i(E_i - E)^2\right) d\beta \tag{11.18}$$

$$dS = -k_B\beta\left(\sum_i p_i(E_i - E)^2\right) d\beta \tag{11.19}$$

These equations may be used in several ways. Note that all first-order variations are expressed as a function of $d\beta$ so it is natural to think of β as the independent variable. But this is not necessary; these equations remain valid no matter which change causes the other changes.

As an example of the insight gained from these equations, note that the formula relating dE and $d\beta$, Equation 11.18, implies that if E goes up then β goes down, and vice versa.

11.2.3   Differential Forms with External Parameters

Now we want to extend these differential forms to the case where the constraint quantities depend on external parameters. In our magnetic-dipole example, the energy of each state depends on the externally applied magnetic field H. Each E_i could be written in the form $E_i(H)$ to emphasize this dependence. Thus the constraint could be written to show this dependence explicitly:

$$E = \sum_i p_i E_i(H) \tag{11.20}$$

Then all the quantities (p_i, α, β, and S) can be thought of as depending on both E and H. In the case of our magnetic-dipole model, the energy $E_i(H)$ happens to be proportional to H with a constant of proportionality that depends on i but not on H. In other models, for other physical systems, E might depend on H or other parameters in different ways.

Consider what happens if both E and H vary slightly, by amounts dE and dH, from the values used to calculate p_i, α, β, and S. There will be small changes dp_i, $d\alpha$, $d\beta$, and dS in those quantities which can be expressed in terms of the small changes dE and dH. The changes due to dE have been calculated above. The changes due to dH enter through the change in the energies associated with each state, $dE_i(H)$ (formulas like the next few could be derived for changes caused by any external parameter, not just the magnetic field).

$$0 = \sum_i dp_i \tag{11.21}$$

$$dE = \sum_i E_i(H)\, dp_i + \sum_i p_i\, dE_i(H) \tag{11.22}$$

$$dS = k_B \beta\, dE - k_B \beta \sum_i p_i\, dE_i(H) \tag{11.23}$$

$$d\alpha = -E\, d\beta - \beta \sum_i p_i\, dE_i(H) \tag{11.24}$$

$$dp_i = -p_i(E_i(H) - E)\, d\beta - p_i \beta\, dE_i(H) + p_i \beta \sum_j p_j\, dE_j(H) \tag{11.25}$$

$$dE = -\left[\sum_i p_i(E_i(H) - E)^2\right] d\beta + \sum_i p_i(1 - \beta(E_i(H) - E))\, dE_i(H) \tag{11.26}$$

$$dS = -k_B \beta \left[\sum_i p_i(E_i(H) - E)^2\right] d\beta - k_B \beta^2 \sum_i p_i(E_i(H) - E)\, dE_i(H) \tag{11.27}$$

For the particular magnetic dipole model considered here, the terms involving $dE_i(H)$ can be simplified by noting that each state's energy $E_i(H)$ is proportional to the parameter H and therefore

$$dE_i(H) = \left(\frac{E_i(H)}{H}\right) dH \tag{11.28}$$

$$\sum_i p_i\, dE_i(H) = \left(\frac{E}{H}\right) dH \tag{11.29}$$

so these formulas simplify to

$$0 = \sum_i dp_i \tag{11.30}$$

$$dE = \sum_i E_i(H)\, dp_i + \left(\frac{E}{H}\right) dH \tag{11.31}$$

$$dS = k_B \beta\, dE - \left(\frac{k_B \beta E}{H}\right) dH \tag{11.32}$$

$$d\alpha = -E\, d\beta - \left(\frac{\beta E}{H}\right) dH \tag{11.33}$$

$$dp_i = -p_i(E_i(H) - E)\left(d\beta + \left(\frac{\beta}{H}\right) dH\right) \tag{11.34}$$

$$dE = -\left[\sum_i p_i(E_i(H) - E)^2\right]\left(d\beta + \left(\frac{\beta}{H}\right) dH\right) + \left(\frac{E}{H}\right) dH \tag{11.35}$$

$$dS = -k_B \beta \left[\sum_i p_i(E_i(H) - E)^2\right]\left(d\beta + \left(\frac{\beta}{H}\right) dH\right) \tag{11.36}$$

These formulas can be used to relate the trends in the variables. For example, the last formula shows that a one percent change in β produces the same change in entropy as a one percent change in H.

11.3   System and Environment

The formulas to this point apply to the system if the summations are over the states of the system, and they also apply to the system and its environment if the summations are over the larger number of states of the system and environment together. (The magnetic-dipole model of Figure 11.1 even shows a system capable of interacting with either of two environments, a feature that is needed if the system is used for energy conversion.) Next are some results for a system and its environment interacting.

11.3.1   Partition Model

Let us model the system and its environment (for the moment consider only one such environment) as parts of the universe that each have their own set of possible states, and which can be isolated from each other or can be in contact. That is, the system, considered apart from its environment, has states which, at least in principle, can be described. Each has an energy associated with it, and perhaps other physical properties as well. This description is separate from the determination of which state is actually occupied—that determination is made using the Principle of Maximum Entropy.

We also assume that the environment has its own set of states, each with its own energy and possibly other physical properties. Again this description of the states is independent of which states are actually occupied.

Our model for the interaction between these two (or what is equivalent, our model for the way the total combination is partitioned into the system and the environment) is that the combination has states each of which consists of one state from the environment and one from the system. Thus, for example, if the system has four states (as our simple two-dipole model does) and the environment has 1000 states, then the combination would have 4000 states. Each state of the combination corresponds to exactly one state of the system and exactly one state of the environment.

We need a notation to keep things straight. We will use the index i for the system and the index j for the environment. Then we can denote the states of the total combination using both i and j, in the form i,j just like the notation for joint probability (which is exactly what it is). A sum over the states of the total combination is then a sum over both i and j.

We will assume that it is possible for the system and the environment to be isolated from one another (the dipole drawing shows a vertical bar which is supposed to represent a barrier to interaction) and then, at other times, for the two to be interacting. Whether they are isolated or interacting does not affect the states or the physical properties associated with the states, although it may affect the probability of occupancy of the states.

11.3.2   Interaction Model

The reason for our partition model is that we want to control interaction between the system and its environment. Different physical systems would have different modes of interaction, and different mechanisms for isolating different parts. Here is described a simple model for interaction of magnetic dipoles that are aligned in a row. It is offered as an example.

Suppose that the apparatus that holds the magnetic dipoles allows adjacent dipoles to influence each other. This influence might be to cause one dipole to change from up to down or vice versa. Naturally, if one dipole influences its neighbor, then its neighbor at the same time influences it. It is reasonable to suppose that if one dipole changes its status from, say, up to down, then the neighbor that is interacting with it should change its status in the opposite direction. The effect is that the two dipoles exchange their orientations. The total number of dipoles oriented in each direction stays fixed.

Consider two adjacent dipoles that exchange their orientations—the one on the left ends up with the orientation that the one on the right started with, and vice versa. There are only a few different cases.

First, if the two dipoles started with the same orientation, nothing would change. On the other hand, if the two dipoles started with different orientations, the effect would be that the pattern of orientations has changed–the upward orientation has moved to the left or the right. This has happened even though the

dipoles themselves have not moved. Since the energy associated with the two possible alignments is different, there has been a small change in the location of the energy, even though the total energy is unchanged.

Second, if both dipoles are in the system, or both are in the environment, then energy may have shifted position within the system or the environment, but has not moved between them.

Third, if the two dipoles started with different alignment, and they are located one on each side of the boundary between the system and the environment, then energy has flowed from the system to the environment or vice versa. This has happened not because the dipoles have moved, but because the orientations have moved.

Energy that is transferred to or from the system as a result of interactions of this sort is referred to as **heat**. A formula for heat in terms of changes of probability distribution is given below.

Sometimes this kind of a process is referred to as "mixing" because the effect is similar to that of different kinds of particles being mixed together. However, in this analogy the dipoles do not move; it is their pattern of orientations or their microscopic energies that have moved and mixed.

Let us assume that we can, by placing or removing appropriate barriers, either inhibit or permit this process. For example, the process might be inhibited by simply moving the system away from its environment physically. Energy conversion devices generally use sequences where mixing is encouraged or discouraged at different times.

11.3.3 Extensive and Intensive Quantities

This partition model leads to an important property that physical quantities can have. Some physical quantities will be called "extensive" and others "intensive."

Whether the system is isolated from the environment or is interacting with it, and whatever the probability distributions $p_{s,i}$ of the system, $p_{e,j}$ of the environment, and $p_{t,i,j}$ of the combination, the energies of the system state and of the environment state add up to form the energy of the corresponding total state (subscripts s, e, and t mean system, environment, and total):

$$E_{t,i,j} = E_{s,i} + E_{e,j} \tag{11.37}$$

The probability of occupancy of total state k is the product of the two probabilities of the two associated states i and j:

$$p_{t,i,j} = p_{s,i} p_{e,j} \tag{11.38}$$

With this background it is easy to show that the expected value of the total energy is the sum of the expected values of the system and environment energies:

$$
\begin{aligned}
E_t &= \sum_{i,j} E_{t,i,j} p_{t,i,j} \\
&= \sum_{i,j} \left[E_{s,i} + E_{e,j} \right] p_{s,i} p_{e,j} \\
&= \sum_i \sum_j \left[E_{s,i} + E_{e,j} \right] p_{s,i} p_{e,j} \\
&= \sum_i p_{s,i} \sum_j E_{e,j} p_{e,j} + \sum_j p_{e,j} \sum_i E_{s,i} p_{s,i} \\
&= \sum_j E_{e,j} p_{e,j} + \sum_i E_{s,i} p_{s,i} \\
&= E_e + E_s \tag{11.39}
\end{aligned}
$$

This result holds whether the system and environment are isolated or interacting. It states that the energy of the system and the energy of the environment add up to make the total energy. It is a consequence

of the fact that the energy associated with each total state is the sum of the energies associated with the corresponding system and environment states.

A quantity with the property that its total value is the sum of the values for the two (or more) parts is known as an **extensive** quantity. Energy has that property, as was just demonstrated. Entropy is also extensive. That is,

$$
\begin{aligned}
S_t &= \sum_{i,j} p_{t,i,j} \ln \left(\frac{1}{p_{t,i,j}} \right) \\
&= \sum_{i,j} p_{s,i} p_{e,j} \left[\ln \left(\frac{1}{p_{s,i}} \right) + \ln \left(\frac{1}{p_{e,j}} \right) \right] \\
&= \sum_i \sum_j p_{s,i} p_{e,j} \left[\ln \left(\frac{1}{p_{s,i}} \right) + \ln \left(\frac{1}{p_{e,j}} \right) \right] \\
&= \sum_i p_{s,i} \sum_j p_{e,j} \ln \left(\frac{1}{p_{e,j}} \right) + \sum_j p_{e,j} \sum_i p_{s,i} \ln \left(\frac{1}{p_{s,i}} \right) \\
&= \sum_j p_{e,j} \ln \left(\frac{1}{p_{e,j}} \right) + \sum_i p_{s,i} \ln \left(\frac{1}{p_{s,i}} \right) \\
&= S_e + S_s
\end{aligned}
\tag{11.40}
$$

Again this result holds whether or not the system and environment are isolated or interacting.

Not all quantities of interest are extensive. In particular, α and β are not. Consider β. This is an example of a quantity for which the values associated with the system, the environment, and the total configuration may or may not be related. If the system and environment are isolated, so that a separate application of the Principle of Maximum Entropy is made to each, then there is no reason why β_s and β_e would be related. On the other hand, if the system and environment are interacting so that they are exchanging energy, the distribution of energy between the system and the environment may not be known and therefore the Principle of Maximum Entropy can be applied only to the combination, not to the system and environment separately. Then, the same value of β would apply throughout.

Quantities like β that are the same throughout a system when analyzed as a whole are called **intensive**.

11.3.4 Equilibrium

The partition model leads to interesting results when the system and its environment are allowed to come into contact after having been isolated. In thermodynamics this process is known as the total configuration coming into equilibrium.

Let us suppose that the system and the environment have been in isolation and therefore are characterized by different, unrelated, values of energy, entropy, and other quantities. Then suppose they are allowed to interact, using a model of interaction in which the total energy is unchanged. Energy may flow from the system to the environment or vice versa because of mixing, and this flow of energy is called heat. As a result, the probabilities of occupancy will change, although the descriptions of the states and their properties, including their energies, do not change.

We have developed general formulas that relate small changes in probabilities, and in E, S, α, and β which can be used now. If the energy of the system is assumed to change somewhat (because of mixing), that fact could be incorporated into a new application of the Principle of Maximum Entropy to the system that would result in modified probabilities, E, S, α, and β. In particular, we saw earlier that the signs of dE and $d\beta$ are opposite, so that if E goes up, β then goes down, and vice versa.

Soon, the transfer of energy between the system and the environment may result in our not knowing the energy of each separately, but only the total energy (which does not change as a result of the mixing). In that case, it would be appropriate to use the Principle of Maximum Entropy on the total combination of

system and environment considered together. When that is done, there will be a new single value of β and a new total entropy. What can be said about these values?

First, the new entropy is the sum of the new entropy of the system and the new entropy of the environment, because entropy is an extensive quantity. Furthermore, the old total entropy (at the time the interaction started) is the sum of the old system entropy and the old environment entropy, for the same reason. However, what is interesting is the new total entropy compared with the old total entropy.

The new entropy, because it is evaluated with the probability distribution that comes from the Principle of Maximum Entropy, is the largest value consistent with the total energy. Any other probability distribution consistent with the same total energy would lead to a smaller (or possibly equal) entropy. One such probability distribution is the distribution prior to the mixing, the one that led to the old entropy value. Therefore the total entropy has increased (or at best stayed constant) as a result of the interaction between the system and the environment. It may be that the entropy of the system alone has gone down, but if so then the entropy of the environment must have gone up at least as much.

The energies of the system and the environment have changed, and as a result the values of β_s and β_e have changed, in opposite directions. Their new values are the same (each is equal to β_t), and therefore this new value lies between the two old values.

11.3.5 Energy Flow, Work and Heat

Let us return to the magnetic dipole model as shown in Figure 11.1.

In this section we will consider interactions with only one of the two environments. In Chapter 12 we will consider use of both environments, which will allow the machine to be used as a heat engine or refrigerator.

Consider first the case that the system is isolated from its environment, as shown in Figure 11.1 (the vertical bars represent barriers to interaction). The system is in some state, and we do not necessarily know which one, although the probability distribution p_i can be obtained from the Principle of Maximum Entropy. A change in state generally requires a nonzero amount of energy, because the different states have different energies. We can always imagine a small enough change dH in H so that the magnetic field cannot supply or absorb the necessary energy to change state. Then we can imagine a succession of such changes in H, none of which can change state, but when taken together constitute a large enough change in H to be noticeable. We conclude that changing H for an isolated system does not by itself change the state. Thus the probability distribution p_i is unchanged. Of course changing H by an amount dH does change the energy through the resulting change in $E_i(H)$:

$$dE = \sum_i p_i \, dE_i(H) \tag{11.41}$$

This change is reversible: if the field is changed back, the energy could be recovered in electrical or magnetic or mechanical form (there is nowhere else for it to go in this model). Energy flow of this sort, that can be recovered in electrical, magnetic, or mechanical form (or some other forms) is referred to as **work**. If $dE > 0$ then we say that work is positive, in that it was done by the external source on the system; if $dE < 0$ then we say that work is negative, in that it was done on the external source by the system. Naturally, in energy-conversion devices it is important to know whether the work is positive or negative. In many cases simply running the machine backwards changes the sign of the work; this is not always true of the other form of energy transfer, discussed below.

Changes to a system caused by a change in one or more of its parameters, when it cannot interact with its environment, are known as **adiabatic** changes. Since the probability distribution is not changed by them, they produce no change in entropy of the system. This is a general principle: adiabatic changes do not change the probability distribution and therefore conserve entropy.

First-order changes to the quantities of interest were given above in the general case where E and the various E_i are changed. If the change is adiabatic, then dE is caused only by the changes dE_i and the general equations simplify to

$$dp_i = 0 \tag{11.42}$$

$$dE = \sum_i p_i \, dE_i(H) \tag{11.43}$$

$$dS = 0 \tag{11.44}$$

$$d\alpha = -E \, d\beta - \beta \sum_i p_i \, dE_i(H) \tag{11.45}$$

$$0 = \left[\sum_i p_i(E_i(H) - E)^2 \right] d\beta + \beta \sum_i p_i(E_i(H) - E) \, dE_i(H) \tag{11.46}$$

If, as in our magnetic-dipole model, the energies of the states are proportional to H then these adiabatic formulas simplify further to

$$dp_i = 0 \tag{11.47}$$

$$dE = \left(\frac{E}{H} \right) dH \tag{11.48}$$

$$dS = 0 \tag{11.49}$$

$$d\alpha = 0 \tag{11.50}$$

$$d\beta = -\left(\frac{\beta}{H} \right) dH \tag{11.51}$$

Next, consider the system no longer isolated, but instead interacting with its environment. The interaction model permits heat to flow between the system and the environment, and by convention we will say the heat is positive if energy flows into the system from the environment, and negative if the energy flows the other way. Energy can be transferred by heat and work at the same time. Work is represented by changes in the energy of the individual states dE_i, and heat by changes in the probabilities p_i. Thus the formula for dE above becomes

$$dE = \sum_i E_i(H) \, dp_i + \sum_i p_i \, dE_i(H) \tag{11.52}$$

where the first term is heat and the second term is work.

11.3.6 Reversible Energy Flow

We saw in section 11.3.4 that when a system is allowed to interact with its environment, total entropy generally increases. In this case it is not possible to restore the system and the environment to their prior states by further mixing, because such a restoration would require a lower total entropy. Thus mixing in general is irreversible.

The limiting case where the total entropy stays constant is one where, if the system has changed, it can be restored to its prior state. It is easy to derive the conditions under which such changes are, in this sense, reversible.

From the formulas given earlier, specifically Equation 11.23, the change in system entropy is proportional to the part of the change in energy due to heat. Thus

$$dS_s = k_B \beta_s \, dE_s - k_B \beta_s \sum_i p_{s,i} \, dE_{s,i}(H) \tag{11.53}$$

$$= k_B \beta_s \left[dE_s - \sum_i p_{s,i} \, dE_{s,i}(H) \right] \tag{11.54}$$

$$= k_B \beta_s \, dq_s \tag{11.55}$$

where dq_s stands for the heat that comes into the system due to the interaction mechanism.

This formula applies to the system and a similar formula applies to the environment:

$$dS_e = k_B \beta_e \, dq_e \tag{11.56}$$

The two heats are the same except for sign

$$dq_s = -dq_e \tag{11.57}$$

and it therefore follows that the total entropy $S_s + S_e$ is unchanged (i.e., $dS_s = -dS_e$) if and only if the two values of β for the system and environment are the same:

$$\beta_s = \beta_e \tag{11.58}$$

Reversible changes (with no change in total entropy) can involve work and heat and therefore changes in energy and entropy for the system, but the system and the environment must have the same value of β. Otherwise, the changes are irreversible. Also, we noted in Section 11.3.4 that interactions between the system and the environment result in a new value of β intermediate between the two starting values of β_s and β_e, so reversible changes result in no change to β.

The first-order change formulas given earlier can be written to account for reversible interactions with the environment by simply setting $d\beta = 0$

$$0 = \sum_i dp_i \tag{11.59}$$

$$dE = \sum_i E_i(H) \, dp_i + \sum_i p_i \, dE_i(H) \tag{11.60}$$

$$dS = k_B \beta \, dE - k_B \beta \sum_i p_i \, dE_i(H) \tag{11.61}$$

$$d\alpha = -\beta \sum_i p_i \, dE_i(H) \tag{11.62}$$

$$dp_i = -p_i \beta \, dE_i(H) + p_i \beta \sum_j p_j \, dE_j(H) \tag{11.63}$$

$$dE = \sum_i p_i (1 - \beta(E_i(H) - E)) \, dE_i(H) \tag{11.64}$$

$$dS = -k_B \beta^2 \sum_i p_i (E_i(H) - E) \, dE_i(H) \tag{11.65}$$

As before, these formulas can be further simplified in the case where the energies of the individual states is proportional to H

$$0 = \sum_i dp_i \tag{11.66}$$

$$dE = \sum_i E_i(H)\, dp_i + \left(\frac{E}{H}\right) dH \tag{11.67}$$

$$dS = k_B \beta\, dE - k_B \beta \left(\frac{E}{H}\right) dH \tag{11.68}$$

$$d\alpha = -\left(\frac{\beta E}{H}\right) dH \tag{11.69}$$

$$dp_i = -\left(\frac{p_i \beta}{H}\right)(E_i(H) - E)\, dH \tag{11.70}$$

$$dE = \left(\frac{E}{H}\right) dH - \left(\frac{\beta}{H}\right)\left[\sum_i p_i(E_i(H) - E)^2\right] dH \tag{11.71}$$

$$dS = -\left(\frac{k_B \beta^2}{H}\right)\left[\sum_i p_i(E_i(H) - E)^2\right] dH \tag{11.72}$$

These formulas will be used in the next chapter of these notes to derive constraints on the efficiency of energy conversion machines that involve heat.

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6.050J / 2.110J Information and Entropy
Spring 2008