Chapter 13

Temperature

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

In Chapter 9 we discussed the simple case which can be done analytically, 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 and three unknowns, and it is straightforward to express the entropy in terms of one of the unknowns, eliminating 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.

In Chapter 10 we discussed a more general case in which there are many probabilities but only one average constraint, so that the entropy cannot be expressed in terms of a single probability. The method of Lagrange multipliers was used, and provided the summations can be done, a general method of solutions was presented.

In Chapter 12 we looked at the implications of the Principle of Maximum Entropy for physical systems that adhere to the multi-state model motivated by quantum mechanics, as outlined in Chapter 11.

We found that the Lagrange multiplier plays a central role. Its value indicates whether states with high or low energy are occupied (or have a higher probability of being occupied). From it all the other quantities, including the expected value of energy and the entropy, can be calculated.

In this chapter, we will interpret β further, and will define its reciprocal as (to within a scale factor) the temperature of the material. Then we will see that there are constraints on the efficiency of energy conversion that can be expressed naturally in terms of temperature.

13.1 Heat Engine

A heat engine is a machine that extracts heat from the environment and produces work, typically in mechanical or electrical form. As we will see, for a heat engine to function there need to be two different environments available. The formulas below place restrictions on the efficiency of energy conversion, in terms of the different values of Lagrange multipliers β of the two environments. We will derive these restrictions.

First, however, it is useful to start to deal with the reciprocal of β rather than β itself. Recall that β is an intensive property: if two systems with different values of β are brought into contact, they will end up with a common value of β, somewhere between the original two values, and the overall entropy will rise. The same is true of $1/\beta$, and indeed of any constant times $1/\beta$. (Actually this statement is not true if one of the two values of is positive and the other is negative; in this case the resulting value of β is intermediate but

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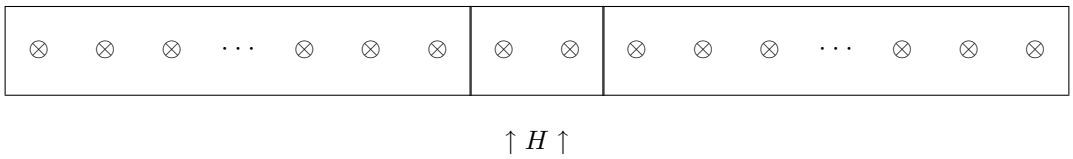

Figure 13.1: Dipole moment example.
(Each dipole can be either up or down.)

the resulting value of $1/\beta$ is not.) Note that $1/\beta$ can, by using the formulas in Chapter 12, be interpreted as a small change in energy divided by the change in entropy that causes it, to within the scale factor k_B.

Let us define the "absolute temperature" as

$$T = \frac{1}{k_B \beta} \tag{13.1}$$

where $k_B = 1.381 \times 10^{-23}$ Joules per Kelvin is Boltzmann's constant. The probability distribution that comes from the use of the Principle of Maximum Entropy is, when written in terms of T,

$$p_i = e^{-\alpha} e^{-\beta E_i} \tag{13.2}$$

$$= e^{-\alpha} e^{-E_i/k_B T} \tag{13.3}$$

The interpretation of β in terms of temperature is consistent with the everyday properties of temperature, namely that two bodies at the same temperature do not exchange heat, and if two bodies at different temperatures come into contact one heats up and the other cools down so that their temperatures approach each other. In ordinary experience absolute temperature is positive, and the corresponding value of β is also. Because temperature is a more familiar concept than Lagrange multipliers, from now on we will express our results in terms of temperature.

The absolute temperature T is expressed in units of Kelvin. The Celsius scale, which is commonly used by the general public in most countries of the world, differs from the Kelvin scale by an additive constant, and the Fahrenheit scale, which is in common use in America, differs by both an additive constant and a multiplicative factor.

For general interest, Table 13.1 shows various temperatures of interest on the three scales, along with β.

	°K	°C	°F	$k_B T = \frac{1}{\beta}$ (J)	β (J^{-1})
Absolute Zero	0	-273.15	-459.67	0	∞
Outer Space (approx)	2.7	-270	-455	3.73×10^{-23}	2.68×10^{22}
Liquid Helium **bp**	4.22	-268.93	-452.07	5.83×10^{-23}	1.72×10^{22}
Liquid Nitrogen **bp**	77.34	-195.81	-320.46	1.07×10^{-21}	9.36×10^{20}
Water **mp**	273.15	0.00	32.00	3.73×10^{-21}	2.65×10^{20}
Room Temperature (approx)	290	17	62	4.00×10^{-21}	2.50×10^{20}
Water **bp**	373.15	100.00	212.00	5.15×10^{-21}	1.94×10^{20}

Table 13.1: Various Temperatures of interest
bp = boiling point, **mp** = melting point

The magnetic-dipole system we are considering is shown in Figure 13.1, where the two environments are at different temperatures, and the interaction of each with the system can be controlled by having the barriers either present or not (shown in the Figure as present).

Let us rewrite the formulas from Chapter12 with the use of β replaced by temperature. Thus

$$1 = \sum_i p_i \tag{13.4}$$

$$E = \sum_i p_i E_i \tag{13.5}$$

$$S = k_B \sum_i p_i \ln\left(\frac{1}{p_i}\right) \tag{13.6}$$

$$p_i = e^{-\alpha} e^{-E_i/k_B T} \tag{13.7}$$

$$\begin{aligned} \alpha &= \ln\left(\sum_i e^{-E_i/k_B T}\right) \\ &= \frac{S}{k_B} - \frac{E}{k_B T} \end{aligned} \tag{13.8}$$

The differential formulas from Chapter 12 for the case of the dipole model where each state has an energy proportional to H become

$$0 = \sum_i dp_i \tag{13.9}$$

$$dE = \sum_i E_i(H)\, dp_i + \left(\frac{E}{H}\right) dH \tag{13.10}$$

$$TdS = dE - \left(\frac{E}{H}\right) dH \tag{13.11}$$

$$d\alpha = \left(\frac{E}{k_B T}\right)\left[\left(\frac{1}{T}\right) dT - \left(\frac{1}{H}\right) dH\right] \tag{13.12}$$

$$dp_i = p_i \left[\frac{E_i(H) - E}{k_B T}\right]\left[\left(\frac{1}{T}\right) dT - \left(\frac{1}{H}\right) dH\right] \tag{13.13}$$

$$dE = \left[\sum_i p_i (E_i(H) - E)^2\right]\left(\frac{1}{k_B T}\right)\left[\left(\frac{1}{T}\right) dT - \left(\frac{1}{H}\right) dH\right] + \left(\frac{E}{H}\right) dH \tag{13.14}$$

$$TdS = \left[\sum_i p_i (E_i(H) - E)^2\right]\left(\frac{1}{k_B T}\right)\left[\left(\frac{1}{T}\right) dT - \left(\frac{1}{H}\right) dH\right] \tag{13.15}$$

and the change in energy can be attributed to the effects of work dw and heat dq

$$dw = \left(\frac{E}{H}\right) dH \tag{13.16}$$

$$dq = \sum_i E_i(H)\, dp_i \tag{13.17}$$

$$= TdS \tag{13.18}$$

13.2 Energy-Conversion Cycle

Consider the cycle shown on the diagram below. Without loss of generality we can treat the case where H is positive. Assume that the left environment has a temperature T_1 which is positive but less (i.e., a higher value of β) than the temperature T_2 for the right environment (the two temperatures must be different for

the device to work). A simple way to envision the cycle is to consider the plane formed by axes corresponding to S and T of the system. The cycle we are interested in forms a rectangle, with corners marked a, b, c, and d, and sides corresponding to the values S_1, S_2, T_1, and T_2:

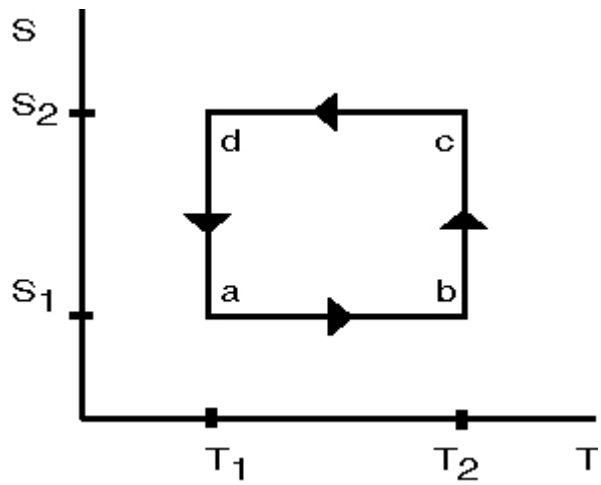

Figure 13.2: Temperature Cycle

Since the temperatures are assumed to be positive, the lower energy levels have a higher probability of being occupied. Therefore, the way we have defined the energies here, the energy E is negative. Thus as the field gets stronger, the energy gets more negative, which means that energy actually gets delivered from the system to the magnetic apparatus. Think of the magnetic field as increasing because a large permanent magnet is physically moved toward the system. The magnetic dipoles in the system exert a force of attraction on that magnet so as to draw it toward the system, and this force on the magnet as it is moved could be used to stretch a spring or raise a weight against gravity, thereby storing this energy. Energy that moves into the system (or out of the system) of a form like this, that can come from (or be added to) an external source of energy is work (or negative work).

First consider the bottom leg of this cycle, during which the temperature of the system is increased from T_1 to T_2 without change in entropy. This is an adiabatic step. By one of the equations above, increasing T is accomplished by increasing H, while not permitting the system to interact with either of its two environments. The energy of the system goes down (to a more negative value) during this leg, so energy is being given to the external apparatus that produces the magnetic field, so the work done on the system is negative.

Next, consider the right-hand leg of this cycle, during which the entropy is increased from S_1 to S_2 at constant temperature T_2. This step, at constant temperature, is called isothermal. According to one of the formulas above, this is accomplished by decreasing H, while the system is in contact with the right environment, which is assumed to be at temperature T_2. During this leg the change in energy E arises from heat, flowing in from the high-temperature environment, and work from the external magnetic apparatus. The heat is $T_2(S_2 - S_1)$ and the work is positive since the decreasing H during this leg drives the energy toward 0.

The next two legs are similar to the first two except the work and heat are opposite in direction, i.e., the heat is negative because energy flows from the system to the low-temperature environment. During the top leg the system is isolated from both environments, so the action is adiabatic. During the left-hand isothermalleg the system interacts with the low-temperature environment.

After going around this cycle, the system is back where it started in terms of its energy, magnetic field, and entropy. The two environments are slightly changed but we assume that they are each so much larger than the system in terms of the number of dipoles present that they have not changed much. The net

change is a slight loss of entropy for the high-temperature environment and a gain of an equal amount of entropy for the low-temperature environment. Because these are at different temperatures, the energy that is transferred when the heat flow happens is different – it is proportional to the temperature and therefore more energy leaves the high-temperature environment than goes into the low-temperature environment. The difference is a net negative work which shows up as energy at the magnetic apparatus. Thus heat from two environments is converted to work. The amount converted is nonzero only if the two environments are at different temperatures.

Table 13.2 summarizes the heat engine cycle.

Leg	Start	End	Type	dS	dT	H	E	Heat in	Work in
bottom	a	b	adiabatic	0	positive	increases	decreases	0	negative
right	b	c	isothermal	positive	0	decreases	increases	positive	positive
top	c	d	adiabatic	0	negative	decreases	increases	0	positive
left	d	a	isothermal	negative	0	increases	decreases	negative	negative
Total	a	a	complete cycle	0	0	0	0	positive	negative

Table 13.2: Energy cycle

For each cycle the energy lost by the high-temperature environment is $T_2(S_2 - S_1)$ and the energy gained by the low-temperature environment is $T_1(S_2 - S_1)$ and so the net energy converted is the difference $(T_2 - T_1)(S_2 - S_1)$. It would be desirable for a heat engine to convert as much of the heat lost by the high-temperature environment as possible to work. The machine here has efficiency

$$\left(\frac{\text{work out}}{\text{high-temperature heat in}}\right) = \frac{T_2 - T_1}{T_2} \tag{13.19}$$

This ratio is known as the Carnot efficiency, named after the French physicist Sadi Nicolas Léonard Carnot (1796 - 1832).[1] He was the first to recognize that heat engines could not have perfect efficiency, and that the efficiency limit (which was subsequently named after him) applies to all types of reversible heat engines.

The operations described above are reversible, i.e., the entire cycle can be run backwards, with the result that heat is pumped from the low-temperature environment to the one at high temperature. This action does not occur naturally, and indeed a similar analysis shows that work must be delivered by the magnetic apparatus to the magnetic dipoles for this to happen, so that more heat gets put into the high-temperature environment than is lost by the low-temperature environment. Heat engines run in this reverse fashion act as refrigerators or heat pumps.

[1] For a biography check out http://www-groups.dcs.st-andrews.ac.uk/~history/Mathematicians/Carnot_Sadi.html