EXERCISE 2.1: EQUILIBRATION OF TWO CAPACITORS (5P)

The entropy of a charged capacitor is given by

$$H(Q) = const + \frac{Q^2}{2Ck_BT},$$

where Q is the charge, C the capacity, k_B the Boltzmann constant, and T is the constant temperature.

(a) Justify this formula using the Clausius relation between differential work and differential entropy $dW = T\,k_B\,\mathrm{d}H$. (1P)

(b) Let us now consider two capacitors (at the same temperature) with the capacities C_1, C_2 which can exchange electric charges, as indicated in the figure. The total electric charge is a conserved quantity. Which "temperature-like" quantity attains the same value in both capacitors after equilibration and what would be the interpretation of this quantity? (1P)

(c) Consider two identical capacitors ($C_1 = C_2 = C$), one of them charged at voltage $U_1 = U$ and the other one discharged ($U_2 = 0$). If they are coupled as in the figure, they will both equilibrate at half of the voltage, i.e. $U_1 = U_2 = U/2$. Compute the entropy change of the two capacitors before and after equilibration. (1P)

(d) Does the result of (c) violate the Second Law? Think about it and compute the entropy production of the entire system during equilibration. (2P)

SAMPLE SOLUTION

(a) The energy of the capacitor is given by

$$E = \frac{1}{2}CU^2 = \frac{1}{2}\frac{Q^2}{C}$$

Therefore, assuming that $\mathrm{d}W \equiv \mathrm{d}E$, we have

$$\mathrm{d}W = \mathrm{d}E = \frac{Q\,\mathrm{d}Q}{C} = k_B\,T\;\mathrm{d}H\,.$$

Integrating this relation on both sides yields the wanted formula:

$$\frac{Q^2}{2C} = k_BT\,H + const$$

(b) Since both systems exchange the conserved quantity Q, the equilibrium state of maximal entropy will be characterized by fluctuations where $\mathrm{d}H_1 = -\,\mathrm{d}H_2$ and $\mathrm{d}Q_1 = -\,\mathrm{d}Q_2$. Therefore the quantity

$$\gamma = \frac{\partial H(Q)}{\partial Q}$$

will attain the same value on both sides, just like temperature attains the same value on both sides in the case of energy exchange. Inserting the above relation and using $Q = CU$ we find that

$$\gamma = \frac{Q}{C\,k_B T} = \frac{U}{k_B T}\,,$$

meaning that our thermodynamic quantity is nothing but the voltage measured at the capacitors. Reaching equilibrium both capacitors have the same voltage, irrespective of the conductivity of the resistor and irrespective of the capacities C_1, C_2. The same happens with two objects coupled by a thermal bridge: they will equilibrate at the same temperature, irrespective of their size and heat capacity and irrespective of the thermal conductivity of the bridge.

Note: A single electron has an electric field but it has no voltage – the notion of 'voltage' does not have any meaning in case of a single electron'. The notion of 'voltage' makes only sense in a complex system. More precisely, the voltage of a complex system (such as a capacitor or a battery) is the price that we have to pay for entropy when trading charges. The charges move in such a way that the total system increases its entropy.

(c) Rewriting $H(Q) = H(U) = const + \frac{CU^2}{2k_BT}$ we find that

$$\begin{aligned} H_{\text{initial}} &= 2const + \frac{CU_0^2}{2k_BT} + 0 \\ H_{\text{final}} &= 2const + 2\frac{C(U_0/2)^2}{2k_BT} \\ \Delta H &= -\frac{CU_0^2}{4k_BT} < 0\,. \qquad ↯ \end{aligned} \tag{1}$$

(d) At first glance the result in (c) is surprising since the entropy change is negative, violating the Second Law. However, we have to take the resistor into account. Elementary calculations show that the voltage at the resistor decays exponentially as $U_R(t) = U_0 e^{-2t/RC}$. This means that the resistor dissipates a heat $\Delta Q = \frac{1}{4}CU_0^2$. This heat is radiated into the environment, increasing its entropy by

$$\Delta H_{env} = \frac{\Delta Q}{k_B T} = \frac{CU_0^2}{4k_BT}$$

This compensates the entropy loss of the capacitors, fortunately restoring the Second Law.

Exercise 2.2: Alternative entropies obeying the Second Law (7P)

Consider a Markov system with configurations $c \in \Omega$ and given rates $w_{c\to c'} \geq 0$. Suppose that the actual probability distribution at time t is $\{p_c(t)\}$. Furthermore, let

$$f : [0,1] \to \mathbb{R}$$

be some function that map the probabilities to a real number.

(a) Let $\langle f \rangle = \sum_c p_c(t) f\big(p_c(t)\big)$ be the expectation value of f at time t. Compute its temporal derivative using the master equation. (2P)

(b) Show that in the case of a closed system, where the rates are known to be symmetric ($w_{c\to c'} = w_{c'\to c}$), the temporal derivative can be expressed as

$$\frac{\mathrm{d}\langle f\rangle}{\mathrm{d}t} = \frac{1}{2}\sum_{c,c'} w_{c\to c'}\Big(p_{c'}(t) - p_c(t)\Big)\Big(g\big(p_c(t)\big) - g\big(p_{c'}(t)\big)\Big)\,,$$

where $g(p) = f(p) + p\,f'(p)$. (1P)

(c) Find a simple sufficient condition on g which ensures that $\langle f\rangle$ obeys a Second Law, meaning that $\frac{\mathrm{d}}{\mathrm{d}t}\langle f\rangle \geq 0$ and $\frac{\mathrm{d}}{\mathrm{d}t}\langle f\rangle = 0$ if and only if the system is in equilibrium. (1P)

(d) Demonstrate that the Shannon entropy and the Tsallis entropy both obey the Second Law. (2P)

(e) Invent a new entropy (find a function f) that satisfies the Second Law. (1P)

Sample Solution

The purpose of this exercise is to show that there are other "entropies" which also satisfy the Second Law. However, these entropies are usually non-extensive (like Tsallis).

(a) Compute derivative:

$$\begin{aligned}\frac{\mathrm{d}\langle f\rangle}{\mathrm{d}t} &= \sum_c \dot{p}_c(t) f\big(p_c(t)\big) + \sum_c p_c(t) f'\big(p_c(t)\big)\dot{p}_c(t) \\ &= \sum_c \dot{p}_c(t)\underbrace{\Big[f\big(p_c(t)\big) + p_c(t) f'\big(p_c(t)\big)\Big]}_{=:\,g(p_c(t))}\end{aligned}$$

where we defined $g(p) = f(p) - pf'(p)$. In this expression we insert the master equation

$$\dot{p}_c(t) = \sum_{c'}\Big(p_{c'}(t)w_{c'\to c} - p_c(t)w_{c\to c'}\Big)$$

where we assume that $c \neq c'$ or, equivalently, that $w_{c\to c} = 0$. We obtain:

$$\frac{\mathrm{d}\langle f\rangle}{\mathrm{d}t} = \sum_{c,c'}\Big(p_{c'}(t)w_{c'\to c} - p_c(t)w_{c\to c'}\Big)g\big(p_c(t)\big)$$

(b) For symmetric rates we have

$$\begin{aligned}\frac{\mathrm{d}\langle f\rangle}{\mathrm{d}t} &= \sum_{c,c'} w_{c\to c'}\Big(p_{c'}(t) - p_c(t)\Big)g\big(p_c(t)\big) \\ &= \frac{1}{2}\sum_{c,c'} w_{c\to c'}\Big(p_{c'}(t) - p_c(t)\Big)\Big(g\big(p_c(t)\big) - g\big(p_{c'}(t)\big)\Big)\end{aligned}$$

(c) Since the rates are non-negative can be chosen freely, it would be sufficient if

$$\Big(p_{c'}(t) - p_c(t)\Big)\Big(g\big(p_c(t)\big) - g\big(p_{c'}(t)\big)\Big) > 0 \qquad \forall c, c'$$

This requires $g(p)$ to be a strict monotonously decreasing function. If the system is not in equilibrium, there is at least pair (c, c') where detailed balance is violated, hence $p_c \neq p_{c'}$ and $w_{c\to c'} > 0$, implying that $\frac{\mathrm{d}\langle f\rangle}{\mathrm{d}t} > 0$. Conversely, in equilibrium all probabilities are equal, hence $\frac{\mathrm{d}\langle f\rangle}{\mathrm{d}t} = 0$.

(d) In the case of Shannon entropy $S = -\sum_c p_c \ln p_c$ we have

$$f(p) = -\ln p \qquad \Rightarrow \qquad g(p) = f(p) + pf'(p) = -1 - \ln p$$

and it is easy to see that $g'(p) < 0$ for all $p \in [0,1]$. In the case of Tsallis entropy

$$S_q \;=\; \frac{1}{1-q}\Big(1 - \sum_c p_c^q\Big) \;=\; \sum_c p_c \frac{1-p_c^{q-1}}{q-1}$$

we get

$$f(p) = \frac{1-p^{q-1}}{q-1} \qquad \Rightarrow \qquad g(p) = \frac{p - qp^q}{p(q-1)}.$$

In order to see whether this function decreases we compute the derivative

$$g'(p) = -qp^{q-2}$$

which is also negative for all $q > 0$.

(e) To solve this problem one invents a monotonously decreasing function $g(p)$ and then solves the differential equation $f(p) + pf'(p) = g(p)$, obtaining the solution $f(p) = \frac{1}{p}\int_0^p g(p)\,\mathrm{d}p$.

- The simplest approach would be to consider a linearly decreasing function, e.g. $g(p) = 1-2p$, giving $f(p) = 1-p$ and therewith the new "entropy" $S = 1 - \sum_c p_c^2$. Up to a constant this is known as "linear entropy" in the literature.
- Similarly, for $f(p) = 1-(n+1)p^n$ we would get $S = 1 - \sum_c p_c^{n+1}$

  Correction advice: Generally we would accept any solution where $g(p)$ decreases and $f(p)$ is correctly integrated up to an integration constant.

(Σ = 12P)