14 Feb.

Recap:

  Entropy

    General $S = -\sum_i p_i \log p_i$

    Micro-canonical   in equil., $S = \log M$

            energy & particle # conserved

  Second law

    Entropy   doesn't decrease, generally increase

        $\rightarrow$ Therm. equilibrium defined by maximal entropy

and subsequently imposing $\sum_i p_i = 1$. Here λ is a parameter called the 'multiplier'. In short, this procedure is valid because $\frac{\partial \overline{S}}{\partial \lambda} = 0$ once we impose $\sum_i p_i = 1$, so that any extremum of $\overline{S}$ corresponds to an extremum of $S = \overline{S}(\lambda = 0)$.

Recalling $\frac{\partial}{\partial x_k} \sum_i f(x_i) = \frac{\partial f(x_k)}{\partial x_k}$, what is the probability p_k that maximizes the modified entropy $\overline{S}$?

$$0 = \frac{\partial \overline{S}}{\partial p_k} = \frac{\partial}{\partial p_k} \left[-\sum_i p_i \log p_i + \lambda \left(\sum_i p_i - 1 \right) \right]$$
$$= -\log p_k - \frac{p_k}{p_k} + \lambda = -\log p_k - 1 + \lambda = 0$$
$$p_k = \exp[\lambda - 1] = const. = \frac{1}{M}$$

You should find that p_k is some constant that depends on λ. We don't care about λ; so long as we know p_k is constant, then we must have $p_k = \frac{1}{M}$ in order to satisfy $\sum_k p_k = 1$. As advertised, we recover Eq. 19 from our new definition of thermodynamic equilibrium based on the second law.

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2.3 Temperature

In the micro-canonical ensemble, the conserved internal energy and particle number are fundamental, while the temperature (like the entropy) is a derived quantity. As discussed below Eq. 20, in thermodynamic equilibrium such derived quantities are functions of the conserved $\{E, N\}$. In this section we will state the definition of temperature for the micro-canonical ensemble and apply this to a spin system. In the next section we will check that our definition reproduces our expectations from everyday experiences.

$T(E, N)$

In thermodynamic equilibrium, the **temperature** $T(E, N)$ in the micro-canonical ensemble is defined by

$S = \log M$

$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_N = \frac{\partial}{\partial E} \log M \bigg|_N \qquad (22)$$

In words, the (inverse) temperature is set by the dependence of the entropy on the internal energy for a fixed number of degrees of freedom.

Since this definition is not terribly intuitive, we will again gain insight by considering N spins in a line, in a magnetic field of strength H. We saw above

that $E = -H(n_+ - n_-)$ for n_+ and $n_- = N - n_+$ spins respectively pointing up and down. With N fixed, each (conserved) value of E defines a *different* micro-canonical system, which we can expect to have a different number of micro-states $M(E)$, different entropy $S(E)$ and different temperature $T(E)$. We will compute the functional forms of each of these three quantities, starting with $M(E)$.

Even though the total energy E remains fixed as time passes, individual spins can 'flip' between pointing up or down. Such spin flips simply have to come in pairs so that the overall $n_\pm$ both remain the same. As illustration, what are representative spin configurations that produce the minimal energy $E_{\text{min}} \equiv E_0$ and the next-to-minimal E_1? What are E_0 and E_1 in terms of $\{N, H\}$, and how many distinct micro-states are there for each of E_0 and E_1?

$$M(E_0) = 1 \qquad\qquad M(E_1) = N = \binom{N}{1}$$

$$H \mid \text{↑↑↑↑↑↑} \qquad\qquad \text{↑N↑↑} \quad \text{↑↑↑↓↑↑} \quad \text{↑↑↑}$$

$$E_0 = -NH \qquad\qquad E_1 = -(N-1)H + H$$
$$= -(N-2)H$$

Your results should generalize to

$$\binom{N}{n_-} = M(E_{n_+}) = \binom{N}{n_+} = \frac{N!}{n_+! \, (N - n_+)!}. \qquad (23)$$

with $n_-!$ noted under $(N-n_+)!$.

To take the derivative in Eq. 22, we need to express n_+ in terms of $\{E, N\}$. It will also be convenient to avoid the factorial operation, which is inconvenient to differentiate. For $N \gg 1$, we can accomplish both these goals by treating the spin system as a random walk (in the space of its possible energies E) and applying the central limit theorem:

- Each spin adds to $x \equiv \frac{E}{-H} = 2n_+ - N$ a 'step' of fixed 'length' ± 1. Our task therefore coincides with the special case we considered in Section 1.5.

- We don't impose any preference for positive vs. negative energies, meaning $p = q = \frac{1}{2}$ in the terminology of Section 1.5.

- With $p = q = \frac{1}{2}$, every one of the 2^N possible configurations of N spins is equally probable. Therefore the probability P_{n_+} that our overall 'walk' ends up producing a configuration with $n_+ = \frac{1}{2}(x + N)$ is simply the fraction of those 2^N states with this n_+, in which we can recognize Eq. 23:

  $E(n_-)$

  $$P_{n_+} = \frac{1}{2^N}\binom{N}{n_+} = \frac{M(E_{n_+})}{2^N} \qquad\Longrightarrow\qquad M(E_{n_+}) = 2^N P_{n_+}.$$

- To estimate P_{n_+} for $N \gg 1$, we apply the central limit theorem just as in Section 1.5.3. In particular, we can re-use our computation that $\mu = 2p - 1 = $ $p = \frac{1}{2}$

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$$x^2 = \left(\frac{\epsilon}{H}\right)^2$$

$$\frac{E}{-H} = x = 2 \cancel{N}_{n_+} - N$$

0 and $\sigma^2 = 4pq = 1$, to find

$$p(x) \approx \frac{1}{\sqrt{2\pi N}} \exp\left[-\frac{x^2}{2N}\right] = \frac{1}{\sqrt{2\pi N}} \exp\left[-\frac{E^2}{2NH^2}\right]$$

for the probability *distribution* from which we want to extract P_{n_+}.

- We saw in Section 1.4 that $P_{\text{const}}(n_+) = p(2n_+ - N)\Delta n_+$ is a good approximation, and $\Delta n_+ = 1$. Therefore we find

$$M(E) = 2^N p(2n_+ - N) \approx \frac{2^{N \cdot}}{\sqrt{2\pi N}} \exp\left[-\frac{E^2}{2NH^2}\right]. \tag{24}$$

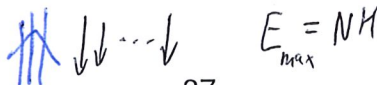What is the derivative of the log of Eq. 24 with N fixed?

$$\left.\frac{\partial}{\partial E}\log M\right|_N = \frac{\partial}{\partial E}\left(-\frac{E^2}{2NH^2} + E\text{-indep.}\right)_N$$

$$= -\frac{E^2}{NH^2} = \frac{1}{T}$$

You should find the temperature

$$T \approx -\frac{NH^2}{E} \qquad N \gg 1, \tag{25}$$

which in several ways does *not* seem to match our expectations from everyday experiences: This T diverges as $E \to 0$ for $n_+ \approx n_-$, and it is negative whenever $n_+ < n_-$ to produce $E > 0$. You can check that this $T < 0$ corresponds to the number of micro-states decreasing for larger internal energies, $\frac{\partial M}{\partial E} < 0$. In so-called *natural* systems, larger energies make more micro-states accessible, producing $\frac{\partial M}{\partial E} > 0$ and a positive temperature. When $H = 0$, we also have $E = 0$ and T is ill-defined.

Restricting our attention to positive temperatures with $H > 0$ and $n_+ > n_-$, we also see that this temperature cannot vanish. It is minimized by the most-negative energy you found above, $T_{\text{min}} = H > 0$ for $E_{\text{min}} = -NH$. The non-zero minimum temperature is specific to spin systems, while some of the other oddities result from the micro-canonical approach more generally. This will motivate turning to the canonical ensemble in Unit 3, but first we can check that some aspects of the micro-canonical temperature defined in Eq. 22 do match our everyday expectations, at least in the 'natural' positive-temperature regime.

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2.4 Heat exchange

From Eq. 25 for the temperature of micro-canonical spin systems, we can see that 'natural' positive temperatures correspond to negative energies, and therefore increase as the energy increases by becoming less negative (with a smaller magnitude). Such a direct relation between energy and temperature is very generic, and we will study it in more detail when considering thermodynamic cycles in a few weeks. For now, considering unspecified systems that exhibit this natural behaviour, let's ask what would happen if we take two initially isolated micro-canonical systems — Ω_A and Ω_B with temperatures T_A and T_B in thermodynamic equilibrium — and bring them into thermal contact.

In micro-canonical terms, the temperatures T_A and T_B are derived from the corresponding energies E_A and E_B, while thermal contact allows the two systems to exchange energy (but not particles) as non-isolated subsystems of a combined micro-canonical system Ω_C. Once the two subsystems have been in thermal contact long enough for the combined system to have reached thermodynamic equilibrium, it will have temperature T_C. We can then re-isolate the two subsystems, which will now have energies E'_A and E'_B with (in thermodynamic equilibrium) temperatures T'_A and T'_B. This three-step procedure is illustrated below.
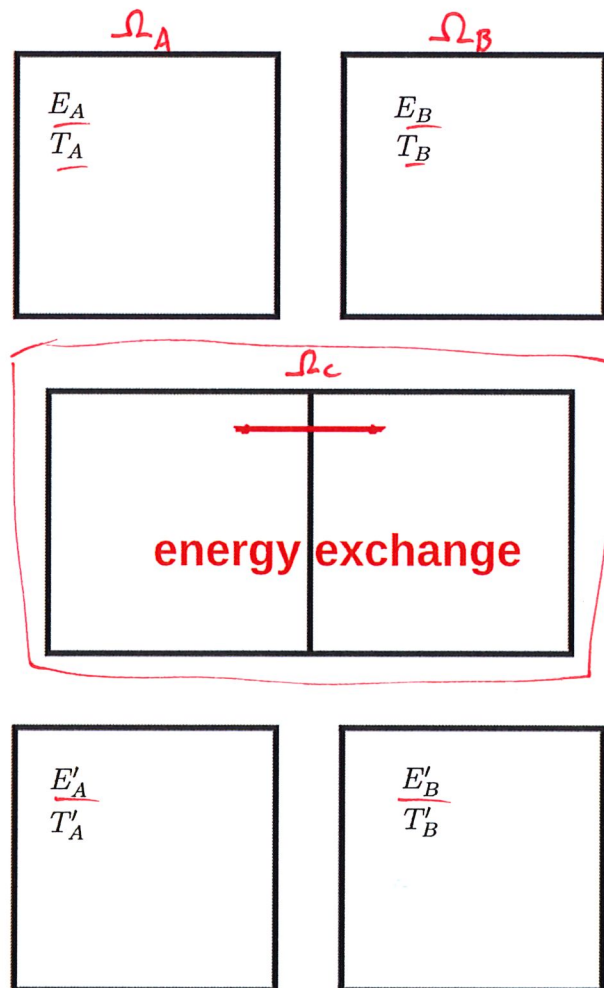
From everyday experience, we expect that this energy exchange will result in a net flow of energy from the hotter system to the colder system, cooling the former by heating the latter. We will now check that the micro-canonical definition of temperature in Eq. 22 predicts this expected behaviour. We define

$$E'_S = E_S + \Delta E_S \qquad \left| \frac{\Delta E_S}{E_S} \right| \ll 1 \qquad S \in \{A, B\},$$

for simplicity considering the case where the change in energy is relatively small. We also know $\Delta E_B = -\Delta E_A$ thanks to conservation of energy.

Equation 22 tells us that we need to consider the entropies as functions of E_S and E'_S in order to connect the temperatures to any flow of energy. Because we don't change the number of particles in each system, we only need to consider the energy dependence of the entropy. We assume $S(E)$ is continuous and infinitely differentiable,[5] which allows us to expand each of the final entropies $S(E'_S)$ in a Taylor series,

$$S(E'_S) = S(E_S + \Delta E_S) \approx S(E_S) + \left. \frac{\partial S}{\partial E} \right|_{E_S} \Delta E_S,$$

neglecting all $\mathcal{O}\left(\Delta E_S^2\right)$ terms because we consider relatively small changes in energy. What is the expression above in terms of the initial temperatures T_S?

$$\left. \frac{\partial S}{\partial E} \right|_{E_s} = \frac{1}{T} \qquad \rightarrow \qquad S(E'_s) \approx S(\!\!\!/ E_s) + \frac{\Delta E_s}{T_s} \quad \Leftarrow$$

From the second law of thermodynamics, we know that the total entropy of these systems can never decrease as time passes:

$$S(E_A) + S(E_B) \leq S(E_A + E_B) = S(E'_A) + S(E'_B). \tag{26}$$

The final equality means that re-isolating the two subsystems doesn't change the entropy. This is because E'_A is not fixed and could take any value from zero to $E_A + E_B$ at the moment when the subsystems are re-isolated. Computing the final entropy $S(E'_A) + S(E'_B)$ therefore requires summing over all possible values of E'_A, producing exactly the sum in Eq. 21 for the overall system. We will see something similar when we consider the 'Gibbs paradox' in Unit 4.

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[5]This assumption breaks down at a *first-order phase transition*, where we would need to be more careful. We will learn about phase transitions towards the end of the term.

What do you find when you insert your linearized Taylor series into Eq. 26?

$$S(E_A') + S(E_B') \approx \cancel{S(E_A)} + \frac{\Delta E_A}{T_A} + S(E_B) + \frac{\Delta E_B}{T_B} \geq \cancel{S(E_A)} + S(E_B)$$

$$\frac{\Delta E_A}{T_A} + \frac{\Delta E_B}{T_B} \geq 0 \;\Rightarrow\; \left(\frac{1}{T_A} - \frac{1}{T_B}\right) \Delta E_A \geq 0$$

$$\Delta E_A = -\Delta E_B$$

Applying conservation of energy should produce

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right) \Delta E_A \geq 0.$$

Recalling from Section 2.2.3 that equality holds only in extremely special cases, we can identify three possibilities consistent with this result. If $T_A > T_B$, then $\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$ is negative and we will generically have $\Delta E_A < 0$, so that energy flows out of the hotter system Ω_A and into the colder one. Our restriction to natural systems means this flow of energy reduces the higher temperature, and increases the lower temperature, bringing the temperatures of the two subsystems closer to each other. Similarly, if $T_A < T_B$, we will generically have $\Delta E_A > 0$, meaning that energy still flows from the hotter system Ω_B into the colder one, again reducing the difference in their temperatures. We can finally conclude that $T_A = T_B$ is the very special case where there is no energy flow, $\Delta E_S = 0$, keeping the temperatures the same. All of this is exactly what we would expect based on our everyday experience of temperature as an intensive quantity.