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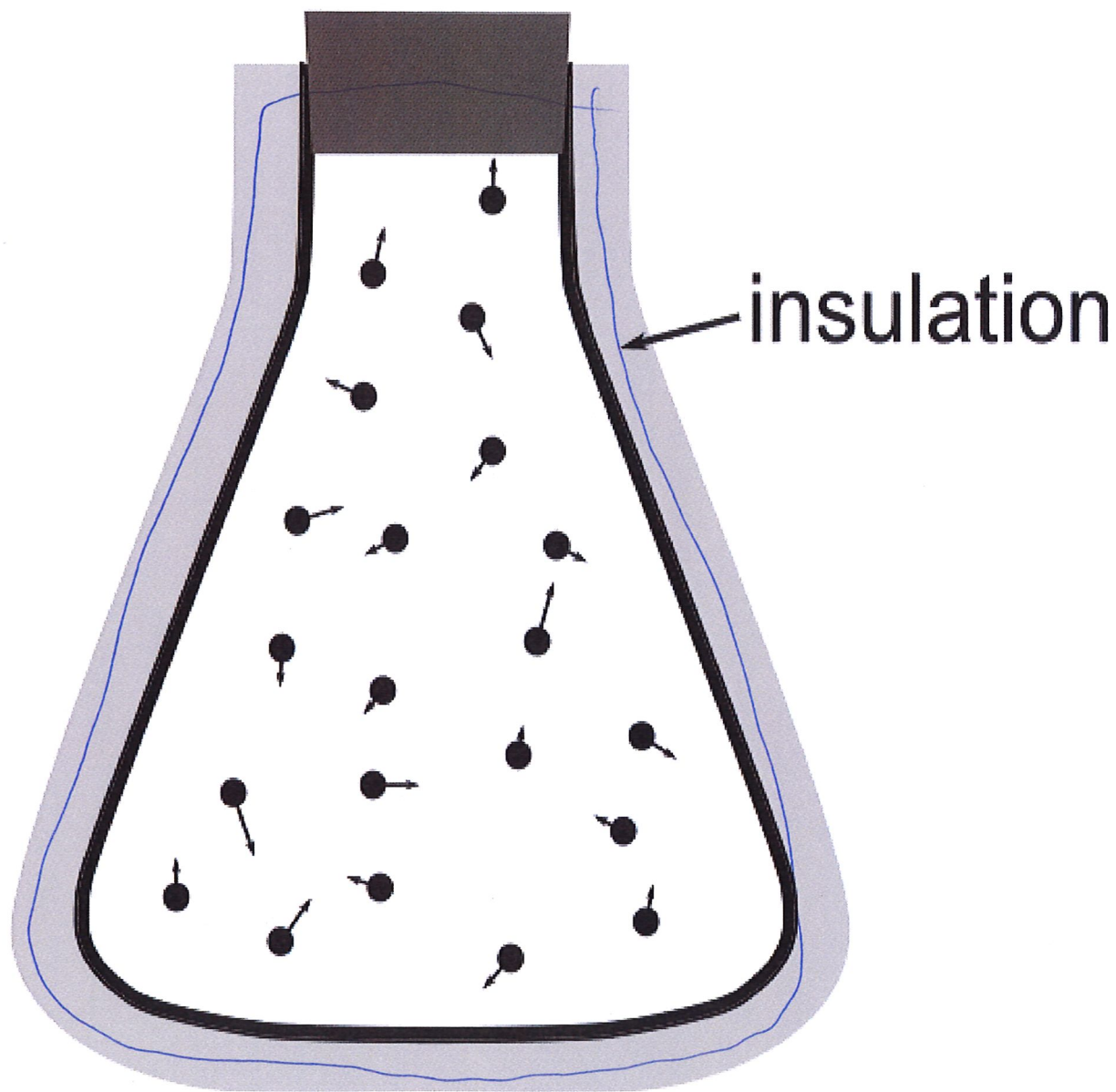
Recap:

Stat. ensembles as prob. spaces

Time evolution of D.o.F ("particles")
probab. listically sample states $w \in \Omega$

Equilibrium \rightarrow characterized by conserved quantities

Micro-canonical \rightarrow energy & particle
'first law'



**Microcanonical
(const. N E)**

2.2 Entropy and its properties

2.2.1 Definition of entropy

We can gain further insight into thermodynamic equilibrium by considering a famous derived quantity.

The **entropy** of a statistical ensemble Ω with a countable number of micro-states M is defined to be

$$S = - \sum_{i=1}^M p_i \log p_i, \quad (20)$$

where p_i is the probability for micro-state ω_i to occur. Unless otherwise specified, "log" indicates the natural logarithm with base e .

When the system under consideration is in thermodynamic equilibrium, we expect derived quantities such as the entropy to be stable over time, even as different micro-states are probabilistically adopted. This implies that such derived quantities are functions of the conserved quantities that are the same for all micro-states. Therefore, for the micro-canonical ensemble, the equilibrium entropy $S(E, N)$ is a function of the conserved energy and particle number.

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By inserting Eq. 19 into Eq. 20 you can quickly compute a simple expression for the entropy of a micro-canonical ensemble in thermodynamic equilibrium:

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$$S = - \sum_{i=1}^M \frac{1}{M} \log \frac{1}{M} = - \log \frac{1}{M} = \log M$$

Boltzmann's Eq.

$$p_i = \frac{1}{M}$$

Your result should depend only on the number of micro-states M , and diverge as $M \rightarrow \infty$. While the energy E and particle number N are not explicit in this expression, $\{E, N, M\}$ are inter-related and might be expressed in terms of each other depending on the particular situation under consideration. For example, what is the equilibrium entropy of the system of N spins considered above, if the magnetic field is turned off, $H = 0$? What is the entropy if $E = 0$ with $H > 0$ (which requires $n_+ = n_-$)?

$2n_+ = N$

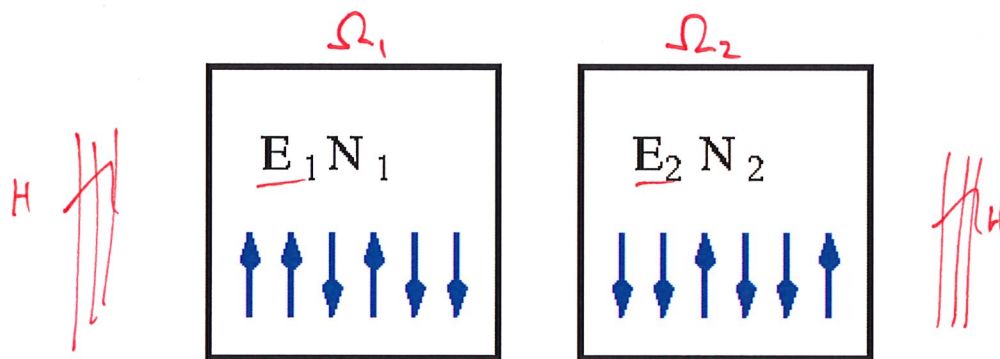
$$S = \log M = \log 2^N = N \log 2 \quad (H=0 \rightarrow E=0)$$

$$H>0, E=0 \quad S = \log M = \log \binom{N}{n_+} = \log \left[\frac{(2n_+)!}{(n_+!)^2} \right] = \log [(2n_+)!] - 2 \log (n_+!)$$

$$N=8 \quad H=0: S = \log(256) \quad \left| \quad H>0 \quad S = \log \left[\frac{8 \cdot 7 \cdot 6 \cdot 5}{4 \cdot 3 \cdot 2} \right] = \log(70)$$

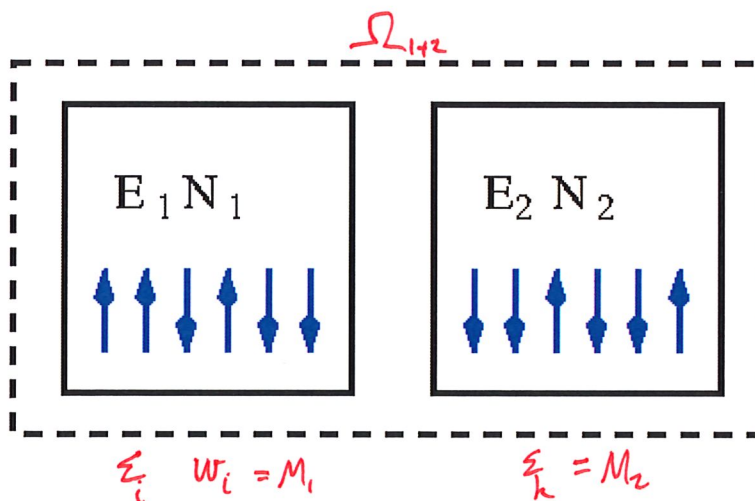
2.2.2 Extensivity

The increase in entropy for an increasing number of micro-states M is a reflection of entropy being an extensive quantity. Extensive quantities are formally defined by considering how they behave if two isolated systems are *analyzed* as a single system—while still remaining isolated from each other, exchanging neither energy nor particles. This is clearest to consider through the specific example shown below of two isolated spin systems, Ω_1 & Ω_2 , respectively characterized by the corresponding energies E_1 & E_2 and particle numbers N_1 & N_2 . To simplify the subsequent analysis, we can assume that both systems are placed in magnetic fields with the same H , so that $E_S = -H(n_+^{(S)} - n_-^{(S)})$ for $S \in \{1, 2\}$.



We can take system Ω_1 to have M_1 micro-states with probabilities p_i while system Ω_2 has M_2 micro-states with probabilities q_k . As discussed above, each M_S is determined by E_S and N_S . Then the entropies of the two systems are

$$S_1 = - \sum_{i=1}^{M_1} p_i \log p_i \qquad S_2 = - \sum_{k=1}^{M_2} q_k \log q_k.$$



Now we keep these two (sub)systems isolated from each other, but consider them as a combined system Ω_{1+2} , as illustrated above. In order to compute the entropy S_{1+2} , we need to figure out the number of micro-states M_{1+2} the combined

system could possibly adopt, and then determine the corresponding probability for each micro-state. Both steps are simplified by the systems being isolated from each other, so that they are statistically independent. Specifically, with subsystem Ω_1 in any one of its M_1 micro-states $\omega_i^{(1)}$, subsystem Ω_2 could independently inhabit any of its M_2 micro-states, implying $M_{1+2} = M_1 M_2$.

Similarly, statistical independence means that the combined probability of subsystem Ω_1 adopting micro-state $\omega_i^{(1)}$ while subsystem Ω_2 adopts $\omega_k^{(2)}$ is the product of the individual probabilities, $p_i q_k$. We can check that this is a well-defined probability, with

$$\sum_{M_{1+2}} p_i q_k = \sum_{i=1}^{M_1} \sum_{k=1}^{M_2} p_i q_k = \left[\sum_{i=1}^{M_1} p_i \right] \cdot \left[\sum_{k=1}^{M_2} q_k \right] = 1 \cdot 1 = 1$$

Inserting the probability $p_i q_k$ into Eq. 20, and recalling $\log(a \cdot b) = \log a + \log b$, what is the combined entropy S_{1+2} of these two independent subsystems?

$$S_{1+2} = - \sum_{i,k} p_i q_k \log(p_i q_k) = - \sum_i p_i \log p_i \sum_k q_k - \sum_k q_k \log q_k \sum_i p_i$$

\downarrow $\log p_i + \log q_k$

$$= S_1 + S_2$$

You should find that the total entropy is just the sum of the entropies of the two isolated systems, which is also how the energies and particle numbers behave,

$$E_{1+2} = E_1 + E_2$$

$$N_{1+2} = N_1 + N_2.$$

This behaviour identifies the energy, particle number and entropy as **extensive quantities**, which are **defined** to be those that add up across independent subsystems. This can be contrasted with **intensive quantities**, which are **defined** to be independent of the extent of the system, and hence the same (on average) for subsystems as for the combined system. **Temperature** and density are everyday examples of intensive quantities, though we will see below that the micro-canonical approach introduces some subtleties. It is possible for quantities to be neither extensive nor intensive: $M_{1+2} = M_1 M_2$ is an example we've already seen.

Finally, suppose that each subsystem is independently in thermodynamic equilibrium, with finite M_1 and M_2 , implying

$$p_i = \frac{1}{M_1}$$

$$q_k = \frac{1}{M_2}$$

$$S_1 = \log M_1$$

$$S_2 = \log M_2.$$

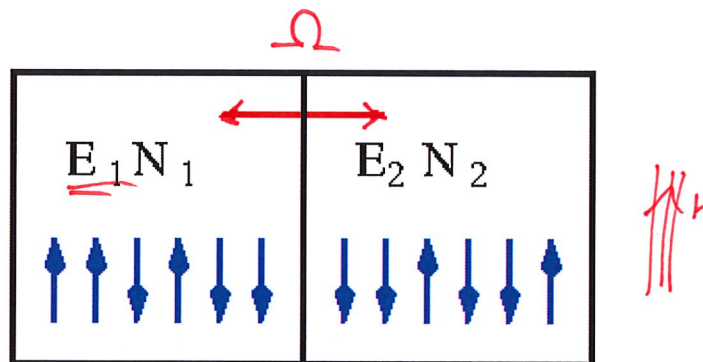
As a consequence we can show that Ω_{1+2} is also in thermodynamic equilibrium, since the probabilities

$$p_i q_k = \frac{1}{M_1 M_2} = \frac{1}{M_{1+2}}$$

are identical every one of its micro-states. In this situation it's even easier to see $S_{1+2} = \log(M_1 M_2) = \log M_1 + \log M_2 = S_1 + S_2$.

2.2.3 Second law of thermodynamics

Let's continue considering the two spin (sub)systems discussed above, with one significant change: We suppose the two subsystems are now able to exchange energy (but not particles) with each other. We'll say they are in thermal contact with each other, rather than being fully isolated. We'll also wait long enough after establishing thermal contact for the combined system to reach equilibrium. This is illustrated by the figure below:



The total energy $E = E_1 + E_2$ remains conserved, so the overall system Ω is still governed by the micro-canonical ensemble. However, the individual energies E_1 and E_2 can now change as time passes, meaning that each subsystem is no longer micro-canonical.

The overall Ω is not the same as the combined Ω_{1+2} considered above. We need to reconsider the total number of micro-states M that Ω could adopt, which is much more difficult than before because we can no longer apply statistical independence. Our key remaining tool is the conservation of the total energy E .

Considering a micro-state in which the N_1 spins contribute energy e_1 to the total, we know that the N_2 spins must contribute the remaining $E - e_1$. Our work above implies there are $M_{e_1} = M_{e_1}^{(1)} M_{E-e_1}^{(2)}$ micro-states providing this particular distribution of energies, where $M_{e_1}^{(1)}$ is the number of micro-states of the formerly isolated subsystem Ω_1 with energy e_1 , and $M_{E-e_1}^{(2)}$ similarly corresponds to Ω_2 with energy $E - e_1$. We also know that it's possible to have $e_1 = E_1$, since that's the initial energy of Ω_1 before it was brought into thermal contact with Ω_2 . When $e_1 = E_1$, we have $M_{E_1} = M_1 M_2$, covering all the micro-states of the combined Ω_{1+2} when the two subsystems were isolated. In addition, we also have to count

any other micro-states for which $e_1 \neq E_1$:

$$\underline{M} = \sum_{e_1} M_{e_1}^{(1)} M_{E-e_1}^{(2)} = \underline{M_1 M_2} + \sum_{\substack{e_1 \neq E_1}} M_{e_1}^{(1)} M_{E-e_1}^{(2)} \geq M_1 M_2. \quad (21)$$

Equality holds when $e_1 = E_1$ is the only possibility, which is an extremely special case (in which the two subsystems remain individually micro-canonical, with fixed E_1 and E_2). This is all we can say in full generality, without specifying more details of a particular example, but it allows us to obtain a famous result for the total entropy S of Ω in *thermodynamic equilibrium*:

$$\underline{S} = \log M \geq \log (M_1 M_2) = \underline{S_{1+2}}.$$

This is a form of the **second law of thermodynamics**,

$$S \geq S_{1+2} = S_1 + S_2.$$

In words, whenever initially isolated (sub)systems in thermodynamic equilibrium are brought into thermal contact with each other and allowed to exchange energy, the total entropy of the overall system can never decrease. Indeed, it generically increases except in extremely special cases.

Though we won't go through a more general derivation here, it turns out that the total entropy never decreases (and generically increases) as time passes, under *any* circumstances. This has many far-reaching consequences, the first of which is a more general definition of thermodynamic equilibrium that (unlike Eq. 19) will also apply when we consider statistical ensembles other than the micro-canonical ensemble. For simplicity we assume that any system under consideration has a finite number of micro-states, which means that its entropy is bounded from above. To motivate the definition below, note that the overall system Ω may have undergone an equilibration process to reach its thermodynamic equilibrium after its two (independently equilibrated) subsystems were brought into thermal contact—and in this process the entropy was non-decreasing.

$$p_i = \frac{1}{M}$$

A system is defined to be in **thermodynamic equilibrium** if its entropy is maximal.

We can *derive* Eq. 19 from this definition. All we need to do is maximize the entropy $S = -\sum_i p_i \log p_i$ subject to the three micro-canonical constraints of conserved energy, conserved particle number, and well-defined probabilities $\sum_i p_i = 1$. It turns out that only the final constraint needs to be incorporated into the maximization, through the method of Lagrange multipliers. As a reminder, this method involves maximizing the modified entropy

$$\underline{\bar{S}}(\lambda) = \underline{S} + \lambda \left(\sum_{i=1}^M p_i - 1 \right) = - \sum_{i=1}^M p_i \log p_i + \lambda \left(\sum_{i=1}^M p_i - 1 \right),$$

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

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 \bar{S} ?

$$\begin{aligned}
 0 = \frac{\partial \bar{S}}{\partial p_k} &= \frac{\partial}{\partial p_k} \left[- \sum_i p_i \log p_i + \lambda \left(\sum_i p_i - 1 \right) \right] \\
 &= - \log p_k - \frac{p_k}{p_k} + \lambda = - \log p_k - 1 + \lambda = 0 \\
 p_k &= \exp[\lambda - 1] = \text{const.} = \frac{1}{M}
 \end{aligned}$$

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.

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

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_N \tag{22}$$

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

$$M = \sum_{e_1} M_{e_1}^{(1)} M_{E-e_1}^{(2)}$$

$$M_{\max} \equiv \max_{e_1} \left(M_{e_1}^{(1)} M_{E-e_1}^{(2)} \right)$$

$$M_{\max} \leq M \leq N_{\text{terms}} \cdot M_{\max}$$

Can be relatively tight bound on M

Suppose N DoF

Can expect $\max(M_{e_1}^{(1)} M_{E-e_1}^{(2)}) \sim e^N$

" $N_{\text{terms}} \sim N$

$$N \sim 10^{23} \quad \therefore \quad \exp(10^{23}) \lesssim M \lesssim 10^{23} \exp(10^{23})$$

$$\text{Entropies:} \quad 10^{23} \lesssim S \lesssim 10^{23} + \log(10^{23}) = 10^{23} + 50 \approx 10^{23}$$

Example:

Ω_1 : $N=10$ spins in mag. field $w/H=1 = \Omega_2$

$$E_1 = -\sum (2n_+^{(1)} - N)$$

$$E_2 = -\sum (2n_+^{(2)} - N)$$

Bring into thermal contact, fix $E_1 + E_2 = -10$

What are inequalities $S_{\min} \leq S_{\text{true}} \leq S_{\max}$?

What if $N=20, 40, \dots$ in each Ω_1, Ω_2 ($E=-10$)