RECAP

Experiment

measurements : events → Maths

Output space
Event space $\{ \omega_1, \omega_2, \ldots \omega_i \ldots \}$ (time evolution)

probability p_2 p_i dim = M

Statistical ~~ensemble~~ ensemble:

☒ particular system: thermodyn. equil.

→ $p_i = 1/M \quad \forall i$

☒ S (conserved quant.)

general: $S = \sum_{i=1}^{M} p_i \ln p_i$

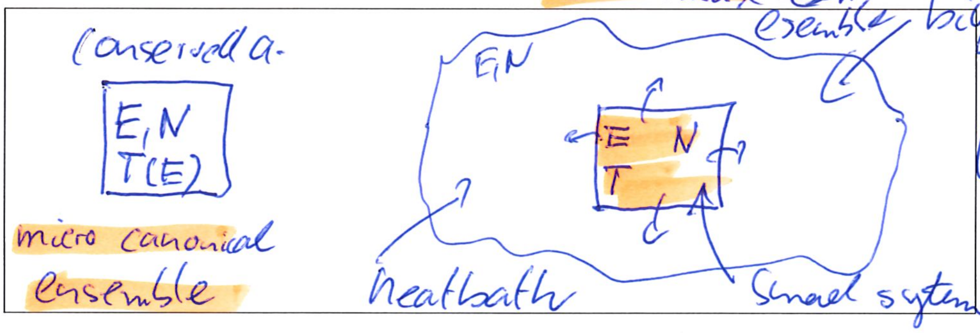
therm. : $S(E,N) = \ln M$

Lectures 11 Feb, 13-15:00

4 The canonical ensemble and Boltzmann's distribution

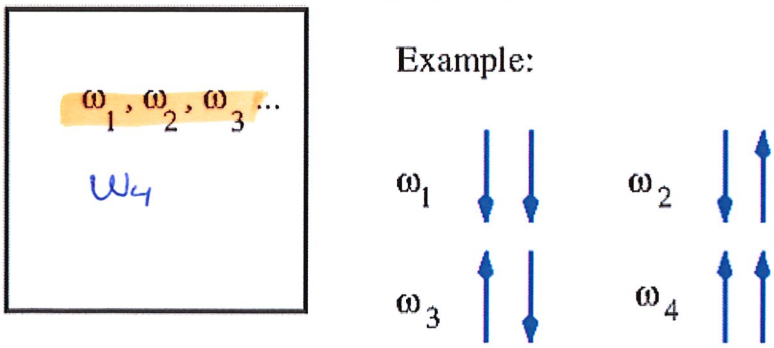
4.1 The heat-bath

Explicit calculations with the microcanonical ensemble are generically difficult. A practical way out is to consider the statistical system in that we are interested immersed into a heat-bath of temperature T, say the surrounding. We view our system as small with a number of degrees of freedom much smaller than that of the surrounding system. If we add our system to the heat-bath, its contribution to the total internal energy is small. When everything has equilibrated, our system will have to a good extent the same temperature T as the heat-bath initially. Canonical ensemble



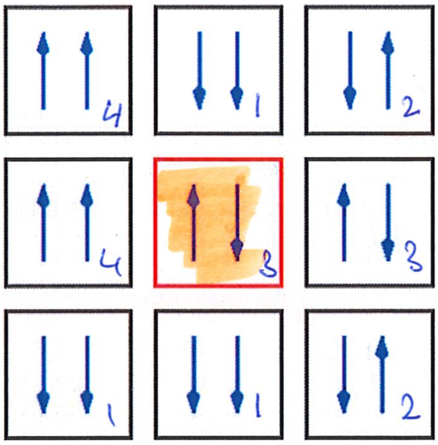
T: temperature characteristics
E: no longer fixed

The "small" system has states $\omega_1, \omega_2, \ldots \omega_M$, which have energies E_i, $i = 1, 2, \ldots$. For example, consider a system consisting of only two spins (see adjacent graph). In this case, our small system has only $M = 4$ states.



The heat-bath is made of the same material, in the above example "spins". In order to get a technical grip on the heat-bath, we consider $N - 1 \gg 1$

replicas of our "small" system. All these systems are allowed to exchange energy and after a while are in thermodynamical equilibrium.



To describe the whole system, we adopt a new way to describe it: we introduce n_i as the number of times that we find ω_i in one of the N boxes.

For the above example, we find:

ω_1: $n_1 = 3$ $\qquad$ $\omega_2 = \downarrow\uparrow$ $n_2 = 2$

$\uparrow\downarrow = \omega_3$ $n_3 = 2$ $\qquad$ $\omega_4 = \uparrow\uparrow$ $n_4 = 2$

↑ boxes with state ω_3

$M=4$: $\sum_{i=1}^{4} n_i = N$

Definition: The n_is are called `occupation numbers`.
Observation: If we pick a box at random, the probability to find a state ω_i in this box is given by $p_i = n_i/N$.

$n_k = 5$ means that 5 boxes out of the N boxes contain state ω_k. Thus, if we sum up all the occupation numbers, we recover that total number N of boxes:

$$\sum_{i=1}^{M} n_i = N. \tag{13}$$

What is the internal energy of the system?

We have n_k states ω_k in system each is contributing the energy E_k to the total internal energy E. Hence, we find:

$$\sum_{k=1}^{M} n_k \, E_k \; = \; E \,. \tag{14}$$

It turns out that E is entirely specified by the occupation numbers, which make them convenient parameters to describe the whole system.

The next step is to find the temperature T for a given total energy E. Since the system is in thermodynamical equilibrium, we just need to find the total number of states M_{all} (Note that M is already reserved for the numer of states in one box). Assume that we have a given set of occupation numbers n_i. If for example $n_1 = 3$, we know that we have state 1 three times in the system but we do not have specified *where* to find those three states. In fact, we have

$$\begin{pmatrix} N \\ n_1 \end{pmatrix} = \frac{N!}{n_1! \, (N - n_1)!}$$

possibilities to find a home for those n_1 states. We now need to distribute n_2 states to the remaining $N - n_1$ slots. For this we have

$$\begin{pmatrix} N - n_1 \\ n_2 \end{pmatrix} = \frac{(N - n_1)!}{n_2! \, (N - n_1 - n_2)!}$$

possibilities. We then continue to distribute n_3 states and so on. The total number of states is therefore:

$$\begin{aligned} M_{all} &= \begin{pmatrix} N \\ n_1 \end{pmatrix} \begin{pmatrix} N - n_1 \\ n_2 \end{pmatrix} \ldots = \frac{N!}{n_1! \, (N - n_1)!} \, \frac{(N - n_1)!}{n_2! \, (N - n_1 - n_2)!} \ldots \\ &= \frac{N!}{n_1! \, n_2! \, \ldots \, n_M!} \,. \end{aligned}$$

The entropy is therefore given by:

$$S(E) = \ln(N!) - \sum_{i=1}^{M} \ln(n_i!) \,.$$

Note that the E dependence enters via the contraint (14). In any macroscopic application the occupation numbers (and N) are fairly large numbers. To give the scale, 22.4litres of gas under normal conditions contains $N_A = 6.022 \times 10^{23}$ molecules, which is just the number of degrees of freedom. N_A is `Avogadro's number` . The number of potential states is usually much larger than the number of degrees of freedom. We therefore going to use the famous `Stirling` approximation for the factorials (see tutorial):

$$\ln(n!) = n \ln n - n + \mathcal{O}(\ln n) .$$

We can neglect the $\ln n$ trem when it is compared to n. For example, $\ln N_A \approx 54.7$ compared to the order 10^{23}. We find:

$$S(E) = \ln N! - \sum_{i=1}^{M} \ln(n_i!)$$
$$\doteq N \ln N - N + O(\ln N) - \sum_{i=1}^{M} (n_i \ln n_i - n_i)$$
$$= N \ln N - \sum_{i=1}^{M} n_i \ln n_i + O(\ln N)$$

remember: $\sum_{i=1}^{M} n_i = N$

We finally find:

$$S(E) = N \ln N - \sum_{i=1}^{M} n_i \ln n_i + \mathcal{O}(\ln N) .$$

We can further simplify if we switch to occupation probabilities $p_i = n_i/N$ as alternative degrees of freedom. We find:

$$\sum_{i=1}^{M} n_i \ln n_i = N \cdot \sum_{i=1}^{M} \frac{n_i}{N} \ln\left(\frac{n_i}{N} \cdot N\right)$$
$$= N \cdot \sum_{i=1}^{M} \frac{n_i}{N} \left(\ln\left(\frac{n_i}{N}\right) + \ln N\right)$$
$$= N \cdot \sum_{i=1}^{M} \frac{n_i}{N} \ln\left(\frac{n_i}{N}\right) + N \cdot \ln N$$

$$S(E) = - N \cdot \sum_{i=1}^{M} p_i \ln(p_i)$$

Altogether with the constraints (13) and (14), we find:

$$S(E) = -N \sum_{i=1}^{M} p_i \ln p_i \;, \tag{15}$$

$$\sum_{i=1}^{M} p_i = \frac{1}{N} \sum_{i=1}^{M} n_i = 1 \;, \tag{16}$$

$$\sum_{i=1}^{M} p_i \, E_i = \frac{1}{N} \sum_{i=1}^{M} n_i \, E_i = E/N \;. \tag{17}$$

Remember that we are in thermodynamical equilibrium. The Second Law of Thermodynamics then suggest that the entropy is maximal. This is powerful then we now can calculate the occupation probabilities p_i! To this aim, we need to maximise $S(E)$ in (15), but we need to take into account the constraints (16,17). The way to do is is with the method of Lagrange:

$S(E) \to \max \qquad \sum_i p_i = 1 \qquad \sum_i p_i E_i = E/N$

$\bar{S}(E) \to \max \qquad \bar{S}(E) = -N \sum_i p_i \ln p_i + \alpha\left(\sum_i p_i - 1\right) + \beta\left(N \cdot \sum_i p_i E_i - E\right)$

$\frac{\partial \bar{S}}{\partial p_i} = -N \ln p_i - N + \alpha + N\beta \cdot E_i \overset{!}{=} 0$

$p_i = \frac{1}{Z} \cdot \exp(-\beta E_i)$ $\qquad \beta, Z$ constant

The final solution is

$$p_i = \frac{1}{Z} \exp\{-\beta E_i\} \;, \tag{18}$$

where the free parameters Z and β must be chosen to satisfy the constraints. Indeed, (16) implies

$$\sum_{i=1}^{M} p_i = 1 \qquad \sum_{i=1}^{M} \frac{1}{Z} e^{-\beta E_i} = 1$$

$$Z = \sum_{i=1}^{M} e^{-\beta E_i}$$

and thus:

$$Z(\beta) = \sum_{i=1}^{M} \exp\{-\beta E_i\} \ . \qquad (19)$$

Definition: $Z(\beta)$ (19) is called `partition function`. It is a primary quantity in statistical and solid physics, from which many thermodynamical observables can be derived.

The constraint (17) then determines the other parameter $\beta(E)$:

$$\frac{1}{Z(\beta)} \sum_{i=1}^{M} E_i \exp\exp\{-\beta E_i\} = \langle E \rangle(\beta) \stackrel{?}{=} E/N \ . \qquad (20)$$

We can now insert (18) into (15) and derive the entropy as a function of E:

$$S(E) = -N \cdot \sum_i p_i \ln p_i = -N \cdot \sum_{i=1}^{M} \frac{1}{Z} e^{-\beta E_i} \left[-\beta E_i - \ln Z\right]$$

$$= N\beta \left(\frac{1}{Z} \sum_{i=1}^{M} E_i e^{-\beta E_i} \right) + N \cdot \ln Z \left(\sum_{i=1}^{M} \frac{1}{Z} e^{-\beta E_i} \right)$$

E/N (20) $\qquad$ $= 1$ (19)

$$= \beta \cdot E + N \cdot \ln Z$$

And thus, we find:

$$S(E) \,=\, \beta(E)\, E \,+\, N \,\ln Z\Big(\beta(E)\Big) \,. \tag{21}$$

Rather than dealing with the total energy E, which is an extensive quantity and as such would depend on the size of the heat-bath, it is much more intuitive to swap E for the intensive parameter T, i.e., temperature. As before, the connection is made via the relation:

$$\frac{1}{T(E)} = \frac{\partial S(E)}{\partial E} \,.$$

We can now insert (21) into the last equation and carry out a remarkable calculation:

$$S'(E) = \beta'(E)\cdot E + \beta(E)\cdot 1 + N \cdot \frac{\partial}{\partial E} \ln Z(\beta(E))$$

$$\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{Z}\frac{\partial}{\partial \beta}\sum_{i=1}^{M} e^{-\beta E_i} = -\frac{1}{Z}\sum_{i=1}^{M} E_i\, e^{-\beta E_i} = -\langle E \rangle$$

$$S'(E) = \beta' E + \beta + N\cdot(-\langle E\rangle)\, \beta'(E) = \beta(E) \overset{!}{=} \frac{1}{T(E)}$$

In summary, we observe:

$$\frac{1}{T(E)} \,=\, \beta(E) \,. \tag{22}$$

Let us scrutinise the mathematical steps to interpret the meaning of the later equation:

- We have calculated the entropy of the whole system as a function of the conserved total energy E. In this process, need to tune $\beta(E)$ to satisfy a constraint.
- We then obtained the temperature $T(E)$ as a function of E. We already said that, for most systems, we can invert this relation providing $E = E(T)$ with, as usual for inverse functions, $T(E(T)) = T$.

- We then define (with a slight recycling of the notation): $\beta(T) := \beta(E(T))$.
- Equation (22) then tells us:

$$\beta(T) = \frac{1}{T} .$$

This is a remarkable result: be switching from the overall conserved energy E to the temperature T, we have severed the connection to the heat-bath: everything can now be calculated as a function T using the states of one "small" system:

$$p_i = \frac{1}{Z(\beta)} \exp\{-\beta E_i\} , \tag{23}$$

$$Z(\beta) = \sum_{i=1}^{M} \exp\{-\beta E_i\} , \qquad \beta = 1/T . \tag{24}$$

DERIVED OBSERVABLES

We are now working with a fixed temperature T, dictated by the heat bath, at the expense that the energy is not conserved since we can exchange energy with the surrounding heat-bath. Hence, the *average internal energy* is a quantity of interest:

$$\langle E\rangle(T) = \frac{1}{Z(\beta)} \sum_{i=1}^{M} E_i \exp\{-\beta E_i\} = -\frac{d}{d\beta} \ln Z(\beta) . \tag{25}$$

We easily show the later equality by noting:

$$\frac{d}{d\beta} \ln Z = \frac{d}{d\beta} \ln \sum_{i=1}^{M} e^{-\beta E_i} = \frac{1}{Z} \frac{d}{d\beta} \sum_{i=1}^{M} e^{-\beta E_i}$$

$$= -\frac{1}{Z} \sum_{i=1}^{M} E_i e^{-\beta E_i} = -\langle E\rangle$$

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

We can also consider the entropy fo our "small" system (rather than that of everything - system and heat-bath:

$$S(T) \;=\; -\sum_{i=1}^{M} p_i \ln p_i \;=\; -\sum_{i=1}^{M} \frac{1}{Z} e^{-\beta E_i} \left[-\beta E_i - \ln Z\right]$$

$$= \beta \frac{1}{Z} \sum_{i=1}^{M} E_i e^{-\beta E_i} + \ln Z$$

$$= \beta \langle E \rangle + \ln Z \, ;$$

Altogether, we find:

$$S(T) \;=\; \beta \, \langle E \rangle(T) \;+\; \ln Z(\beta) \, . \tag{26}$$

Another important quantity is the heat capacity c_v[3].

Key definition: The heat capacity is defined by

$$c_v \;=\; \frac{d}{dT} \, \langle E \rangle \, .$$

Key observation: The heat capacity is always positive (and is only zero in exceptional cases):

$$c_v \;=\; \frac{1}{T^2} \, \left\langle \left(E - \langle E \rangle \right)^2 \right\rangle \;\geq\; 0 \, .$$

(Fluctuation-Dissipation theorem).

The later observation is an example of a so-called `Fluctuation-Dissipation theorem`. The derivation is part of the the homework problems. It is an important result since it reconciles our mathematical approach with everyday life experience: we would expect that, if we raise the temperature, the internal energy $\langle E \rangle$ increases (everything else would very counter intuitive!). Indeed, the theorem is telling us just this: the slope $d\langle E \rangle / dT$ is (generically) positive.

[3]The subscript V later will mean that we keep the volume constant, but we will have to wait until we have introduced V properly below.

4.2 Helmholtz Free Energy

As we have seen, the partition function (24) plays a major role if our system is embedded in a large system at a given temperature. A quantity with the dimensions of energy related to the partition function is the following:

Key definition: if $Z(T)$ is the partition function of a canonical ensemble, the Helmholtz Free Energy is defined by:

$$F(T) = -T \ln Z(T) . \tag{27}$$

KEY PROPERTIES:

We can express the average energy (25) of our ensemble in terms of the temperature T and Free Energy $F(T)$:

$$\langle E\rangle(T) = -\frac{d}{d\beta} \ln Z$$

$$\frac{d}{dT} \ln Z = \frac{1}{Z}\frac{d}{dT} \sum_{i=1}^{M} e^{-E_i/T} = \frac{1}{Z} \sum_{i=1}^{M} \frac{E_i}{T^2} e^{-E_i/T} = \frac{\langle E\rangle}{T^2}$$

$$\langle E\rangle = T^2 \cdot \frac{d}{dT}(\ln Z) = -T^2 \frac{d}{dT}\left(\frac{F(T)}{T}\right) \quad //$$

Likewise, we find from (26) a connection to the entropy:

$$S(T) = \beta \cdot \langle E\rangle + \ln Z$$

$$\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}\left[T \ln Z\right] = -\ln Z - T \frac{\partial}{\partial T} \ln Z$$

$$= -\ln Z - T \frac{\langle E\rangle}{T^2} = -S(T)$$

In summary, we have made

$$S(T) = -\frac{\partial F}{\partial T}$$

Key observations: If $F(T)$ is the Helmholtz Free Energy, we find:

$$\langle E\rangle(T) = -T^2 \frac{d}{dT}\left(\frac{F(T)}{T}\right), \tag{28}$$

$$S(T) = -\frac{d}{dT}F(T). \tag{29}$$

$$\langle E\rangle(T) = T\,S(T) + F(T). \tag{30}$$