18 Feb

Recap: Canonical ensemble
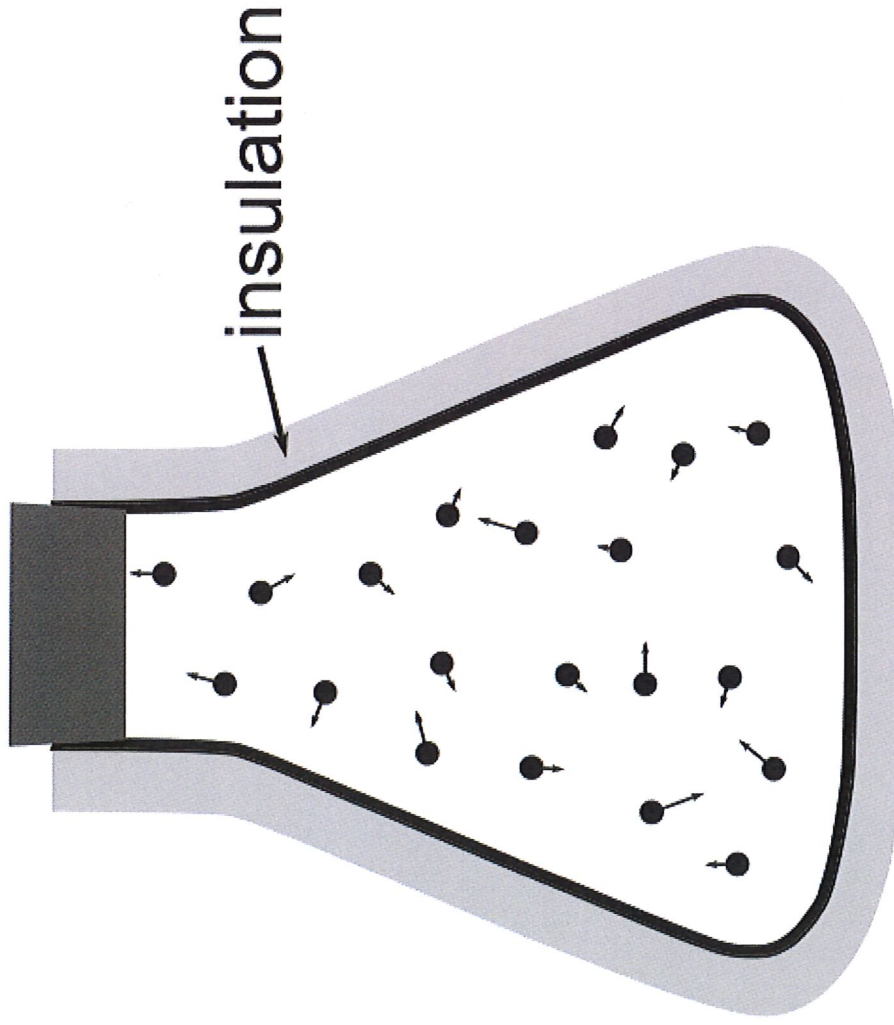
Fix temperature + conservation of total energy

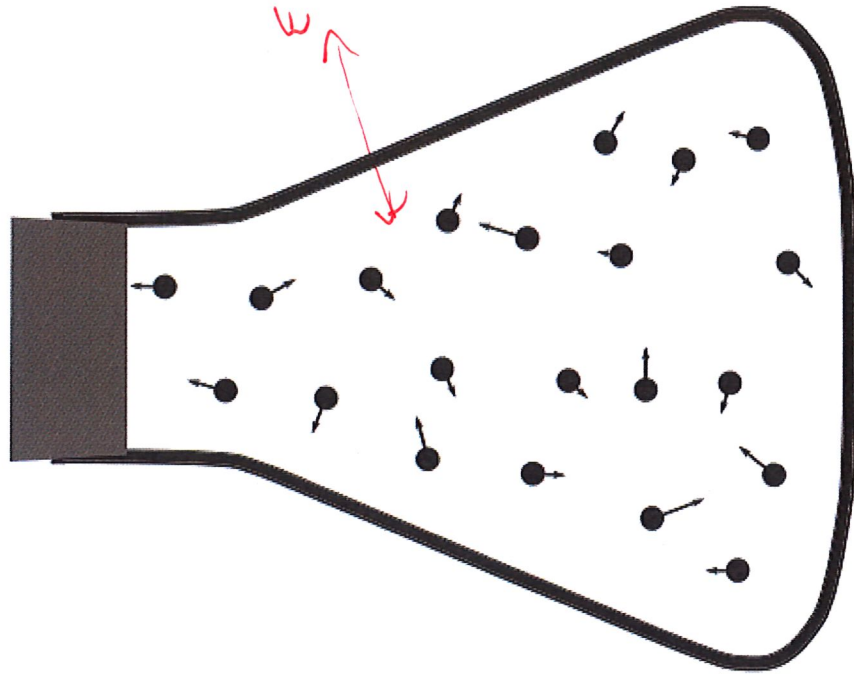$\hookrightarrow$ Thermal reservoir

Replica trick $\rightarrow$ ansatz

Thermal equilibrium by maximizing entropy

$\hookrightarrow$ Partition function $Z = \sum_i e^{-\beta E_i}$

Canonical
(const. N T)

fixed

E

Microcanonical
(const. N E)

conserved

insulation

By defining a new parameter Z in terms of α, you should find

$$p_k = \frac{1}{Z} e^{-\beta E_k}. \tag{29}$$

As before, we need to fix the parameters $\{Z, \beta\}$ by demanding that the two constraints above are satisfied. The first of these constraints is straightforward and produces an important result:

$$1 = \sum_{i=1}^{M} p_i = \frac{1}{Z} \sum_{i=1}^{M} e^{-\beta E_i} \qquad \Longrightarrow \qquad Z(\beta) = \sum_{i=1}^{M} e^{-\beta E_i}. \tag{30}$$

Equation 30 defines the canonical **partition function** $Z(\beta)$, a fundamental quantity in the canonical ensemble, from which many other derived quantities can be obtained.

$Z(\beta)$ still depends on the other as-yet-unknown parameter $\beta(E_{\text{tot}})$. Applying our second constraint, Eq. 27, relates β to E_{tot}:

$$E_{\text{tot}} = R \sum_{i=1}^{M} p_i E_i = \frac{R}{Z(\beta)} \sum_{i=1}^{M} E_i\, e^{-\beta E_i} = R \frac{\sum_{i=1}^{M} E_i\, e^{-\beta E_i}}{\sum_{i=1}^{M} e^{-\beta E_i}}. \tag{31}$$

This relation is a bit complicated, but will suffice for our goal of expressing the entropy in terms of E_{tot}. Inserting Eq. 29 for p_i into your earlier result for the entropy, what do you obtain upon applying Eqs. 30 and 31?

$$S(E_{\text{tot}}) = -R \sum_{i=1}^{M} p_i \log p_i = \quad -R \sum_i p_i \log\left(\frac{1}{Z} e^{-\beta E_i} \right)$$

$$= R \log Z \sum_i p_i + R\beta \sum_i p_i E_i$$

$$= R \log Z + \beta E_{\text{tot}}$$

There is a pleasant simplification when we take the derivative to determine the temperature. Defining $\beta' \equiv \frac{\partial}{\partial E_{\text{tot}}} \beta(E_{\text{tot}})$, we have

$$\frac{1}{T} = \frac{\partial}{\partial E_{\text{tot}}} S(E_{\text{tot}}) = \frac{\partial}{\partial E_{\text{tot}}} [E_{\text{tot}}\beta + R \log Z(\beta)] = \beta + E_{\text{tot}}\beta' + R \frac{1}{Z} \frac{\partial Z(\beta)}{\partial \beta} \beta'.$$

Using Eq. 31 we can compute

$$\frac{1}{Z} \frac{\partial Z(\beta)}{\partial \beta} = \frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{i=1}^{M} e^{-\beta E_i} = -\frac{1}{Z} \sum_{i=1}^{M} E_i\, e^{-\beta E_i} = -\sum_{i=1}^{M} p_i E_i = -\frac{E_{\text{tot}}}{R},$$

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

so that we don't need to figure out the explicit form of β':

$$\frac{1}{T} = \beta + E_{\text{tot}}\beta' - E_{\text{tot}}\beta' = \beta. \tag{32}$$

What's truly remarkable about Eqs. 29, 30 and 32 is that they make no reference to the R replicas or any extensive quantity such as E_{tot} — all information about the thermal reservoir has vanished. This is the goal we have been pursuing since the start of this unit! The large thermal reservoir is still present to fix the temperature T characterizing the canonical system Ω, but beyond that nothing about it is relevant (or even knowable) in the canonical approach. Every aspect of Ω can now be specified in terms of its fixed temperature T and conserved particle number N, starting with the parameter $\beta = 1/T$.

In particular, the partition function from Eq. 30 is simply

$$Z(T) = \sum_{i=1}^{M} e^{-E_i/T}. \tag{33}$$

and together with β specifies the probabilities

$$p_i = \frac{1}{Z} e^{-E_i/T} \tag{34}$$

from Eq. 29. This p_i is now the probability—in thermodynamic equilibrium—that Ω adopts micro-state ω_i with (non-conserved) internal energy E_i. This probability distribution is called either the **Boltzmann distribution** or the **Gibbs distribution**, while $e^{-E_i/T}$ itself is known as a **Boltzmann factor**. All micro-states with the same energy have the same probability in thermodynamic equilibrium, which is consistent with the micro-canonical behaviour we saw in Unit 2.

3.2 Internal energy, heat capacity, and entropy

In addition to fixing the temperature of the system Ω, the thermal reservoir also allows the internal energy of Ω to fluctuate. The system simply exchanges energy with the reservoir, satisfying the first law of thermodynamics. Although the internal energy fluctuates, its expectation value $\langle E \rangle$ is an important derived quantity in thermodynamic equilibrium. Applying the general definition from Eq. 4 to the probability space of the canonical ensemble,

$$\langle E \rangle (T) = \sum_{i=1}^{M} E_i \, p_i = \frac{1}{Z} \sum_{i=1}^{M} E_i \, e^{-\beta E_i}.$$

Here we highlight the dependence of $\langle E \rangle$ on the temperature, and also freely interchange $\beta = 1/T$.

The expression above may look familiar from our work in the previous section:

$$\frac{\partial}{\partial \beta} \log Z = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{Z}\sum_i \frac{\partial}{\partial \beta} e^{-\beta \epsilon_i} = \frac{1}{Z}\sum_i \left(-\epsilon_i\right) e^{-\beta \epsilon_i}$$

$$= -\sum_i \epsilon_i p_i = -\langle E \rangle$$

In this case it is easier to take the derivative with respect to β as opposed to

$$\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = -\frac{1}{\beta^2}\frac{\partial}{\partial T} = -T^2 \frac{\partial}{\partial T}. \tag{35}$$

In Section 2.3, we saw that 'natural' micro-canonical systems exhibit higher (derived) temperatures for larger (conserved) internal energies. Here, in the canonical approach, the average internal energy $\langle E \rangle$ is the derived quantity while the temperature is fixed. From our everyday experience, we expect a similar direct relation between temperature and energy, which the following result confirms.

> The **heat capacity** is defined to be
>
> $$c_v = \frac{\partial}{\partial T}\langle E \rangle, \tag{36}$$
>
> and is always non-negative, $c_v \geq 0$.

The subscript indicates that the volume of the system is kept fixed; we'll consider the role of the volume more carefully starting in Unit 4. In a homework assignment you will confirm $c_v \geq 0$ by deriving a **fluctuation–dissipation** (or **fluctuation–response**) **relation**. That relation will be a special case of a more general theorem, and will connect the fluctuations of the internal energy around its expectation value, $\sum_i \left(E_i - \langle E \rangle\right)^2$, to the energy's *response* to a change in temperature, $\frac{\partial}{\partial T}\langle E \rangle$. Equality will hold only in extremely special cases, meaning that the heat capacity is generically positive, in agreement with our intuition that higher temperatures produce larger internal energies.

We finally need to compute the entropy of Ω with no reference to the thermal reservoir, apart from its role fixing the temperature in thermodynamic equilibrium. Since the general definition of the entropy in Eq. 20 continues to hold for the canonical ensemble, we just need to insert the probabilities p_i from Eq. 34:

$$
\begin{aligned}
S(T) = -\sum_{i=1}^{M} p_i \log p_i &= -\sum_i p_i \log\left(\frac{1}{Z} e^{-\beta E_i}\right) \\
&= +\sum_i p_i \left(+\log Z\right) + \beta \sum_i p_i E_i \\
&= \log Z + \beta \langle E \rangle = \log Z + \frac{\langle E \rangle}{T}
\end{aligned}
$$

You should find that the entropy depends on $\log Z$.

3.3 Helmholtz free energy

This dependence of the entropy on $\log Z$ is in accordance with our earlier claim that the partition function is a fundamental quantity in the canonical ensemble. Recalling from Eq. 33 that Z is a sum over all micro-states, we can view this result as the canonical counterpart to the micro-canonical entropy being the logarithm of the number of micro-states. (Thermodynamic equilibrium is required in both cases.) This motivates the following definition of a quantity with the dimensions of energy that is related to $\log Z$, which provides simpler and more elegant expressions for the derived quantities we considered above.

The **Helmholtz free energy** of a system in the canonical ensemble is

$$
F(T) = -T \log Z(T) \qquad\qquad F(\beta) = -\frac{\log Z(\beta)}{\beta}, \qquad (37)
$$

where Z is the partition function of the system. In terms of this free energy, Eqs. 33 and 34 are

$$
Z = e^{-F/T} \qquad\qquad p_i = e^{(F - E_i)/T}.
$$

$$\frac{\partial}{\partial \beta} = -T^2 \frac{\partial}{\partial T}$$

The Helmholtz free energy is named after Hermann von Helmholtz and reveals its usefulness when we take its derivative. The derivative involves $\frac{\partial}{\partial T} \log Z$, which is worth collecting in advance based on Eq. 35:

$$-\frac{\partial}{\partial T}\left(\frac{F(T)}{T}\right) = \frac{\partial}{\partial T}\log Z(T) = \frac{1}{T^2}\frac{\partial}{\partial \beta}\log Z(\beta) = \frac{\langle E \rangle}{T^2}$$
$$+ \beta \langle E \rangle$$

$$\frac{\partial}{\partial T}F(T) = \frac{\partial}{\partial T}\left(-T \log Z\right) = -\log Z - T\frac{\partial}{\partial T}\log Z$$
$$= \frac{F}{T} - \frac{\langle E \rangle}{T} = -S(T)$$

From these results we can read off the more elegant expressions promised above:

$$S(T) = -\frac{\partial}{\partial T}F(T) \tag{38}$$

$$\langle E \rangle(T) = -T^2 \frac{\partial}{\partial T}\left(\frac{F(T)}{T}\right) = \frac{\partial}{\partial \beta}[\beta F(\beta)] = TS(T) + F(T). \tag{39}$$

3.4 The physics of information

As a first application of the canonical ensemble, we will explore physically observable effects that depend on the pure information content of a statistical system. You may be aware of the importance of information through the famous black hole information paradox, but that topic is well beyond the scope of this module since it involves quantum mechanics and general relativity in addition to statistical physics. Here we will consider simple spin systems as introduced in Section 2.1, contrasting the behaviour of their average internal energy $\langle E \rangle$ and entropy S depending on whether or not the spins can (in principle) be distinguished from each other. It's important to appreciate that the "information" discussed here is an intrinsic property of the system—what is *knowable* about it in principle. It does not matter whether or not any observer actually knows this information; so long as it can possibly be known it will have an effect.

3.4.1 Distinguishable spins in a solid

We begin with the setup from Section 2.1: A system of N spins arranged in a line, placed in an external magnetic field of strength H, and in thermodynamic equilibrium. We further specify that the spins are embedded in a solid material that fixes their positions and prevents them from moving. This allows them to be distinguished from one another: An observer can target an appropriate position in the solid to measure the corresponding spin. The spins distinguished in this
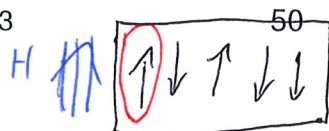
way will be aligned either anti-parallel or parallel to the magnetic field. The canonical system therefore has $M = 2^N$ distinct micro-states ω_i with energies E_i and probabilities $p_i = \frac{1}{Z}e^{-E_i/T}$, each defined by the orientations of all N spins.

To streamline our notation, we can represent the orientation of the nth spin as $s_n \in \{1, -1\}$, where $s_n = 1$ indicates alignment parallel to the field and $s_n = -1$ indicates alignment anti-parallel to the field. Since the spins don't interact with each other, the internal energy of the system in micro-state ω_i specified by the N spins $\{s_n\}$ is therefore

$$E_i = -H \sum_{n=1}^{N} s_n. \tag{40}$$

To compute the canonical partition function Z_D, where the subscript reminds us of the spins' distinguishability, we have to sum over all 2^N possible spin configurations $\{s_n\}$. In this process we can save some space by defining the dimensionless variable $x = \beta H = \frac{H}{T}$:

$$Z_D = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{-\beta E_i} = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\left[x \sum_{n=1}^{N} s_n\right]$$

$$= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{xs_1} \cdots e^{xs_N} = \left(\sum_{s_1=\pm 1} e^{xs_1}\right) \cdots \left(\sum_{s_N=\pm 1} e^{xs_N}\right)$$

$$= \left(\sum_{s=\pm 1} e^{xs}\right)^{N} = \left(e^x + e^{-x}\right)^N = \left[2\cosh\left(\beta H\right)\right]^N, \tag{41}$$

distributing the summations since all the spins are independent of each other.

The corresponding Helmholtz free energy

$$F_D(\beta) = -\frac{\log Z(\beta)}{\beta} = -\frac{N \log\left[2\cosh\left(\beta H\right)\right]}{\beta} \tag{42}$$

18 Feb.

is all we need to compute the average internal energy:

$$\langle E \rangle_D = \frac{\partial}{\partial \beta}\left[\beta F_D(\beta)\right] =$$

From this we immediately obtain the entropy

$$S_D = \beta\left(\langle E \rangle_D - F_D\right) = -N\beta H \tanh\left(\beta H\right) + N \log\left[2\cosh\left(\beta H\right)\right]. \tag{43}$$

These results for $\langle E \rangle_D$ and S_D are plotted below as functions of $\frac{T}{H} = \frac{1}{\beta H}$. Since both these quantities are extensive, we normalize them by showing $\frac{\langle E \rangle_D}{NH}$ and $\frac{S_D}{N}$.