21 Feb.

Logistics: HW due 3 March

Recap:

Canonical ensemble - fix T, N

↳ Partition function $Z = \sum_i e^{-\beta E_i}$ $\quad \beta = \frac{1}{T}$

Free energy: $F = -T \log Z$

$$\left.\begin{aligned} \langle E \rangle &= \frac{\partial}{\partial \beta}(\beta F) \\ S &= -\frac{\partial}{\partial T} F \end{aligned}\right\}$$

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 $x = \beta H = \frac{H}{T}$:

$$\begin{aligned} Z_D &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{-\beta E_i} = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\left[x \sum_{n=1}^{N} s_n\right] \\ &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{xs_1} \cdots e^{xs_N} = \left(\sum_{s_1=\pm 1} e^{xs_1}\right) \cdots \left(\sum_{s_N=\pm 1} e^{xs_N}\right) \\ &= \left(\sum_{s=\pm 1} e^{xs}\right)^N = \left(e^x + e^{-x}\right)^N = \left[2\cosh(\beta H)\right]^N, \end{aligned} \tag{41}$$

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

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The corresponding Helmholtz free energy

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

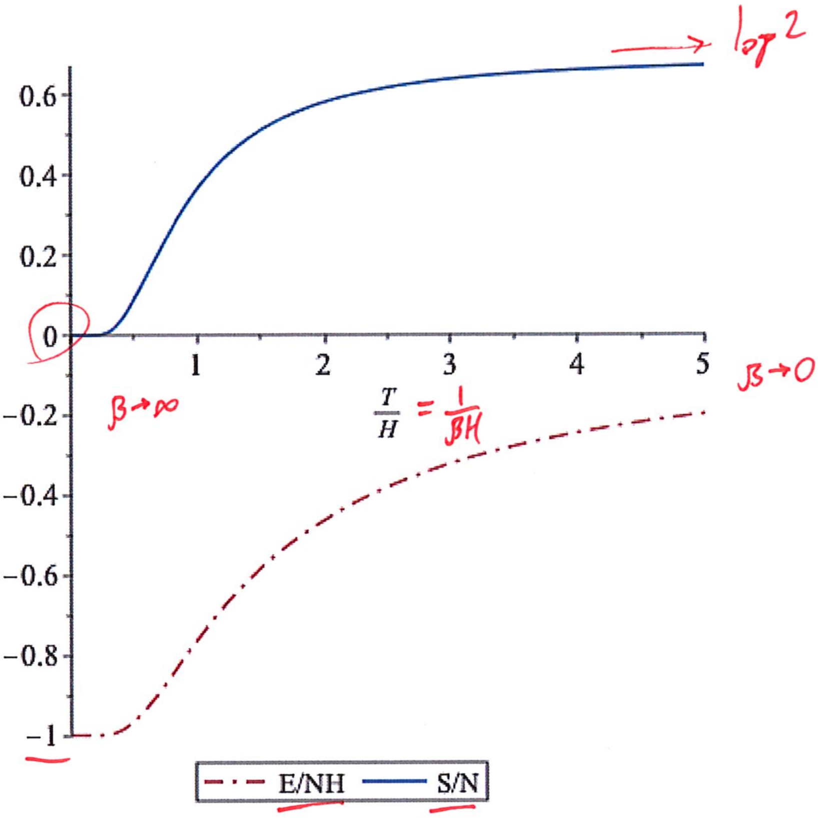
is all we need to compute the average internal energy:

$$\begin{aligned} \langle E \rangle_D = \frac{\partial}{\partial \beta}\left[\beta F_D(\beta)\right] &= -N \frac{\partial}{\partial \beta} \log\left[2\cosh(\beta H)\right] \\ &= \frac{-N}{2\cosh \beta H}\left(2\sinh(\beta H)\right) H \\ &= -NH\tanh(\beta H) \end{aligned}$$

From this we immediately obtain the entropy

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

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 $\frac{S_D}{N}$.



Let's check the asymptotic behaviour of these functions, starting with **low temperatures**. In contrast to the micro-canonical Eq. 25, in the canonical ensemble there is no issue with taking the independent variable $T \to 0$. This corresponds to $\beta H \to \infty$ and $\tanh(\beta H) \to 1$, approaching the "ground-state" energy $E_{\text{min}} = E_0 = -NH$ you computed in Section 2.3. This energy is only produced by the single micro-state in which all the spins are aligned with the magnetic field, $s_n = 1$ for all n (or $n_+ = N$ and $n_- = 0$ in the notation from Section 2.3). Correspondingly, $\log[2\cosh(\beta H)] \to \log e^{\beta H} = \beta H$ and the two terms in Eq. 43 cancel out, so that $S_D \to 0$. This vanishing entropy is a generic consequence of temperatures approaching *absolute zero.*

$e^{-E_i/T}$

For low but non-zero temperatures, $\langle E\rangle_D$ and S_D will be affected by the non-zero probability for the system to adopt micro-states ω_i with higher energies $E_i > E_0$. These higher-energy configurations are often referred to as "excited states", with the drawback that a single excited state may correspond to many different micro-states. For example, in Section 2.3 you also computed the energy $E_1 = -(N-2)H$ of the first excited state, which is realized by N distinct micro-states (with $n_- = 1$). In the case of spin systems, we can instead refer to *energy levels* that are all separated by a constant *energy gap* $\Delta E \equiv E_{n_-+1} - E_{n_-} = 2H$.

We can compute the effects of the higher energy levels at low temperatures $\beta H \gg 1$ by expanding $\langle E \rangle_D$ in powers of $e^{-\beta H} \ll 1$. What is the first temperature-dependent term in this expansion?

$$\frac{\langle E \rangle_D}{NH} = -\tanh(\beta H) = -\frac{1-e^{-2\beta H}}{1+e^{-2\beta H}} = -(1-e^{-2\beta H})(1-e^{-2\beta H} + \mathcal{O}(e^{-4\beta H}))$$

$$= -1 + 2e^{-2\beta H} + \mathcal{O}(e^{-4\beta H}) \qquad \Delta E = 2H$$

$$= -1 + 2e^{-\Delta E/T} + \mathcal{O}(e^{-4\beta H})$$

You should find that the excited-state effects are *exponentially* suppressed by the energy gap ΔE at low temperatures,

$$\frac{\langle E \rangle_D}{NH} = -1 + 2e^{-\beta\Delta E} + \mathcal{O}\left(e^{-2\beta\Delta E}\right).$$

This is a generic feature of canonical systems with a non-zero energy gap, and is due to the exponentially suppressed probability for the system to adopt any of the micro-states with the higher energy,

$P_i \propto e^{-\beta E_i}$

$$\frac{\frac{1}{Z}e^{-\beta E_{n_-+1}}}{\frac{1}{Z}e^{-\beta E_{n_-}}} = e^{-\beta\Delta E}.$$

The low-temperature expansion of Eq. 43 for the entropy S_D in powers of $e^{-\beta H} \ll 1$ is similar:

$$\frac{S_D}{N} = \frac{\beta}{N}(\langle E \rangle_D - F) = \frac{H\beta}{\cancel{N}}\left(\cancel{-1} + 2e^{-\beta\Delta E} + \mathcal{O}(e^{-2\beta\Delta E})\right) + \frac{1}{H\beta}\log[2\cosh(\beta H)]$$

$$\log[2\cosh(\beta H)] = \log[e^{\beta H}(1+e^{-2\beta H})] = \cancel{\beta H} + e^{-2\beta H} + \mathcal{O}(e^{-4\beta H})$$

$$\frac{S_D}{N} = \underbrace{2H}_{\Delta E}\beta e^{-\beta\Delta E} + e^{-\beta\Delta E} + \mathcal{O}(e^{-2\beta\Delta E})$$

Here the leading term includes a linear factor of $\beta\Delta E \gg 1$, but this can't overcome the now-expected exponential suppression:

$$\frac{S_D}{N} = \beta\Delta E e^{-\beta\Delta E} + e^{-\beta\Delta E} + \mathcal{O}\left(e^{-2\beta\Delta E}\right).$$

In the limit of **high temperatures** we should instead expand in powers of the small factor $\beta H \ll 1$. This is straightforward for $\langle E\rangle_D$:

$$\frac{\langle E\rangle_D}{NH} = -\tanh\left(\beta H\right) = -\beta H + \frac{\left(\beta H\right)^3}{3} + \mathcal{O}\left([\beta H]^5\right),$$

which vanishes $\sim\frac{1}{T}$ as $T \to \infty$. This matches the micro-canonical behaviour we saw for this system from Eq. 25, where the derived temperature diverged as the conserved energy approached zero.

For the entropy, there is a similar connection to micro-canonical behaviour at high temperatures:

$$\frac{S_D}{N} = \frac{\beta\langle E\rangle_D}{N} - \frac{\beta F}{N} = -(\beta H)^2 + \mathcal{O}(\beta^4 H^4) + \log\left[2\cosh(\beta H)\right]$$

$$\log\left[2\cosh(\beta H)\right] = \log 2 + \log\left[1 + \tfrac{1}{2}(\beta H)^2 + \mathcal{O}(\beta H)^4\right]$$

$$= \log 2 + \cancel{\log}\, \tfrac{1}{2}(\beta H)^2 + \mathcal{O}(\beta^4 H^4)$$

$$\frac{S_D}{N} = \log 2 - \tfrac{1}{2}(\beta H)^2 + \mathcal{O}(\beta^4 H^4)$$

As $\frac{T}{H} \to \infty$, the result

$$\frac{S_D}{N} = \log 2 - \frac{\left(\beta H\right)^2}{2} + \mathcal{O}\left([\beta H]^4\right)$$

approaches the asymptotic value $S_D \to N\log 2 = \log M$ for the $M = 2^N$ micro-states (with different energies). Qualitatively, in this limit the energy of each spin is negligible compared to the temperature, and the system approximately behaves as though the energy were zero for all micro-states (and hence conserved).

3.4.2 Indistinguishable spins in a gas

Next, let's consider nearly the same setup, with N spins in thermodynamic equilibrium, in an external magnetic field of strength H. The only difference is that now the spins are allowed to move, like particles in a one-dimensional gas. We demand that they move slowly so that we can ignore their kinetic energy and the total energy of the system continues to be given by Eq. 40. Since the spins don't interact with each other, they can freely move past each other, and even occupy the same space, making it impossible for them to be distinguished from one another in any way.

To compute the fundamental canonical partition function (Eq. 33), we have to sum over the micro-states of the system. These micro-states are no longer in one-to-one correspondence with the full configurations $\{s_n\}$ of the N spins. Because the spins are now indistinguishable, certain spin configurations also cannot be distinguished from each other. The simplest example comes from the two-spin system considered in Section 3.1.1, where the configurations $\downarrow\uparrow$ and $\uparrow\downarrow$ now both map onto a single micro-state. In this micro-state, we know only that one spin is $s_i = 1$ while the other is $s_k = -1$; it's not possible to distinguish which is which.

Generalizing, we can conclude that a single distinct micro-state corresponds to all possible permutations of spins with fixed $\{n_+, n_-\}$. This means that each micro-state is now in one-to-one correspondence with the energy $E = -H(n_+ - n_-)$, which we can organize as energy levels separated by a constant energy gap $\Delta E = 2H$. As a quick example, enumerate the energy levels when $N = 4$ and list the spin configurations associated with the corresponding micro-states. How many micro-states are there for N spins?

Micro-states	Configs
$E = -4H$	$\uparrow\uparrow\uparrow\uparrow$
$-2H$	$\uparrow\uparrow\uparrow\downarrow$ + perms.
0	$\uparrow\uparrow\downarrow\downarrow$ + perms.
$2H$	$\uparrow\downarrow\downarrow\downarrow$ + perms.
$4H$	$\downarrow\downarrow\downarrow\downarrow$

A convenient way to label these micro-states and energy levels is to define

$$E_k = -NH + 2Hk = -H(N - 2k)$$

for micro-state ω_k with $k = n_- = 0, \cdots N$. To compute the partition function Z_I, with the subscript reminding us about the spins' indistinguishability, we now have

$$Z_I = \sum_{k=0}^{N} e^{-\beta E_k} = \sum_{k=0}^{N} e^{\beta H(N-2k)} = e^{N\beta H} \sum_{k=0}^{N} \left(e^{-2\beta H}\right)^k = e^{N\beta H} \frac{1 - e^{-2(N+1)\beta H}}{1 - e^{-2\beta H}}. \quad (44)$$

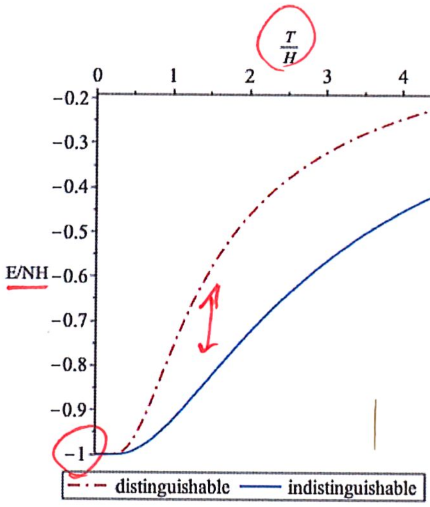
The geometric series in the last step can be reconstructed by considering

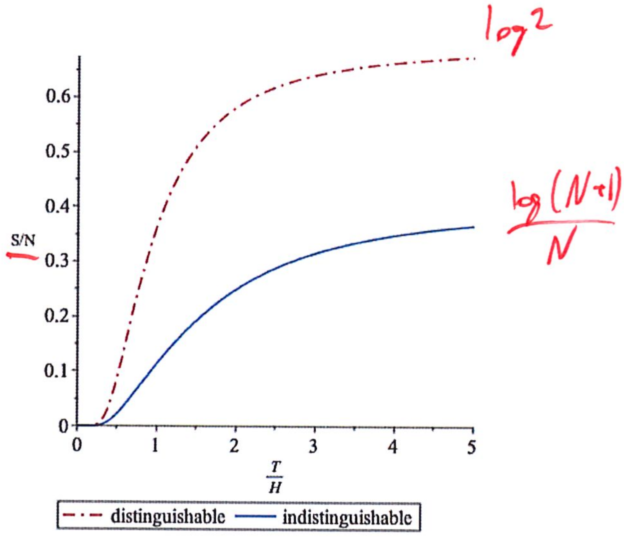
$$\sum_{k=0}^{N} x^k = \sum_{k=0}^{\infty} x^k - \sum_{k=N+1}^{\infty} x^k = \frac{1}{1-x} - x^{N+1} \sum_{\ell=0}^{\infty} x^\ell = \frac{1}{1-x} - \frac{x^{N+1}}{1-x}.$$

The corresponding Helmholtz free energy is

$$F_I(\beta) = -\frac{\log Z(\beta)}{\beta} = -NH - \frac{\log\left[1 - e^{-2(N+1)\beta H}\right]}{\beta} + \frac{\log\left[1 - e^{-2\beta H}\right]}{\beta}. \quad (45)$$

In contrast to Eq. 42, $F_I(\beta)$ is no longer proportional to N. In a homework assignment you will use F_I to determine the average internal energy $\langle E \rangle_I$ and entropy S_I shown in the figures below, and also check the low- and high-temperature expansions like we did for the distinguishable case above. Unlike our results for the distinguishable case, you will find that $\frac{\langle E \rangle_I}{NH}$ and $\frac{S_I}{N}$ depend on N, which requires us to fix $N = 4$ in the plots below.





The dash-dotted lines in these figures are exactly the distinguishable-spin results we previously discussed. The solid lines are the new results for indistinguishable spins. We see that the same $T \to 0$ limits are approached in both cases: $E \to -NH$ and $S \to 0$. At low temperatures, the indistinguishable results approach these limits more quickly — they still feature exponential suppression of excited-state effects by the energy gap, $\propto e^{-\beta \Delta E}$, but this now comes with additional factors of N.

At high temperatures there is an even more striking difference. While the average internal energy $\langle E \rangle_I$ continues to vanish $\sim \frac{1}{T}$ as $T \to \infty$ (with different N dependence), the entropy approaches the asymptotic value $S_I \to \log(N+1) = \log M$ for the $M = N+1$ micro-states. This logarithmic dependence on N is very different from the $S_D \to N \log 2$ limit we found for distinguishable spins, and reflects the exponentially smaller number of micro-states that exist for indistinguishable spins, $N+1$ vs. 2^N.

Finally, away from those low- and high-temperature limits, the left figure above shows a significant difference in the internal energies of the spin systems, depending only on whether or not the spins can be distinguished from each other in principle. This is a physically measurable effect caused by the intrinsic information content of a statistical system, and a simple illustration of phenomena that remain at the leading edge of ongoing research. The conclusion was memorably stated by Rolf Landauer in 1991: "Information is physical."