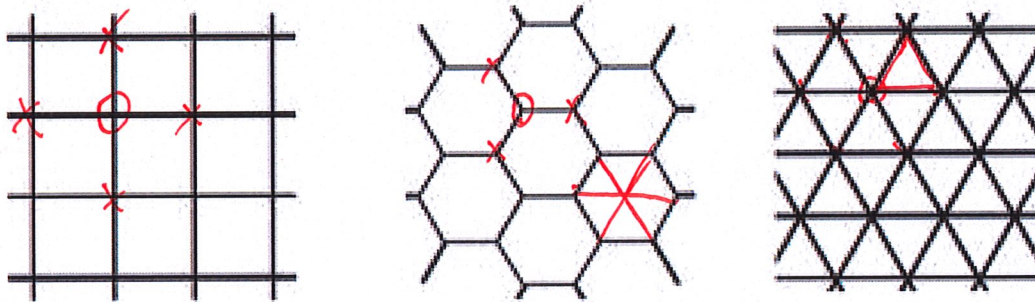


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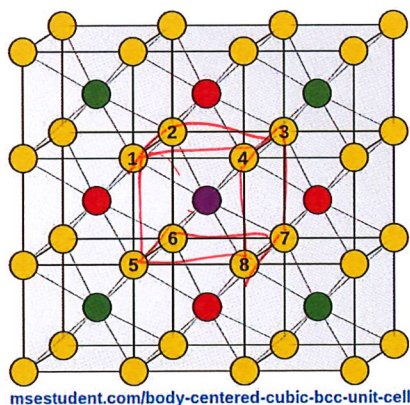
Tutorial problem — Lattices

In the module we are focusing on simple cubic lattices with periodic boundary conditions, but other lattice structures play important roles in both nature and mathematics. Some of the remarkable electronic properties of graphene, for example, are due to its two-dimensional honeycomb lattice structure, while more elaborate three-dimensional lattices play central roles in the search for materials exhibiting high-temperature superconductivity.

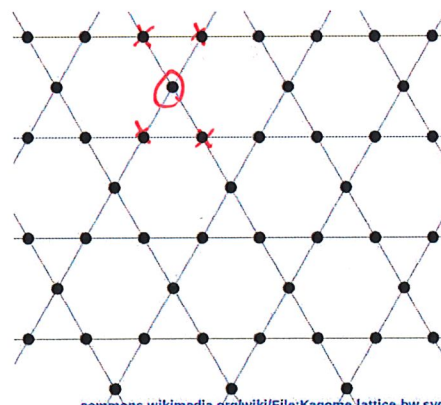
The figure below shows three simple two-dimensional lattices, each of which has a different coordination number — the number of nearest neighbours for each site (with periodic boundary conditions). We have already seen that the square lattice has coordination number $C = 2d = 4$, and generalizes to simple cubic and hyper-cubic lattices in higher dimensions.



The honeycomb lattice of graphene has a smaller coordination number $C = d + 1 = 3$, and generalizes to 'hyper-diamond' lattices in higher dimensions. Finally, the triangular lattice essentially fills in the middle of each honeycomb cell, leading to coordination number $C = 2(d + 1) = 6$. Its higher-dimensional generalizations are known as A_d^* lattices, of which the simplest example is the three-dimensional body-centered cubic lattice shown below. Also shown below is the 'kagome' lattice, which has the same $C = 4$ as the square lattice, illustrating that the coordination number is insufficient to completely characterize a lattice.



mstudent.com/body-centered-cubic-bcc-unit-cell



commons.wikimedia.org/wiki/File:Kagome_lattice-bw.svg

Things become more interesting when we consider generalizing the Ising model to have energy

$$E = -J \sum_{(jk)} s_j s_k - H \sum_{n=1}^N s_n,$$

with nearest neighbours (jk) defined by any of the three simple two-dimensional lattices above. While any positive interaction strength $J > 0$ can be rescaled to $J = 1$ without loss of generality, the case of a constant negative $J < 0$ is qualitatively different. Specializing to $d = 2$ and $H = 0$, let's consider a couple of **conceptual questions**: What are the minimum-energy ground states for each case $J > 0$ and $J < 0$, for each of the square, honeycomb and triangular lattices? Can you think of an order parameter distinguishing these ground states from the disordered micro-states that dominate at high temperatures?

Generalizing the Ising model in this way opens up a vast landscape of possible applications both practical and abstract. As one example (with both practical and abstract relevance), a **spin glass** can be modeled by allowing the interaction strength to vary from site to site,

$$E_{\text{SG}} = - \sum_{(jk)} J_{jk} s_j s_k.$$

Giorgio Parisi was awarded part of the 2021 Nobel Prize in Physics for his work studying the mathematics of such spin glass systems. In particular, he was able to solve the so-called Sherrington–Kirkpatrick model

$$E_{\text{SG}} = - \sum_{j < k} J_{jk} s_j s_k,$$

where the values J_{jk} are randomly drawn from a gaussian distribution around some mean J_0 and the system is defined on a fully connected lattice (or **complete graph**) where every site j is a nearest neighbour of every other site $k \neq j$. (Summing only over $j < k$ and not $j > k$ avoids double-counting the link jk .) As shown on the next page, a fully connected lattice with N sites has $\frac{1}{2}N(N-1) = \binom{N}{2}$ links.

While we may look a bit more closely at spin glasses if time permits during the next couple of weeks, for now let's consider a simpler Ising system with constant interaction strength on the fully connected lattice:



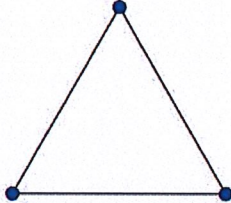
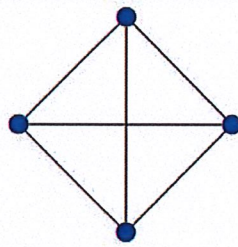
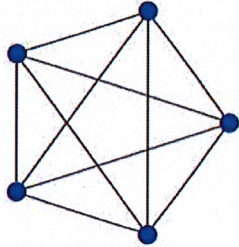
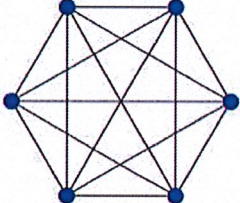
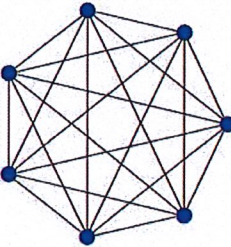
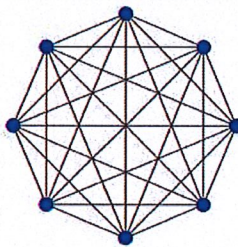
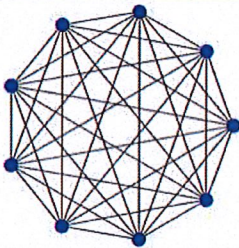
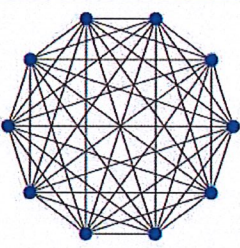
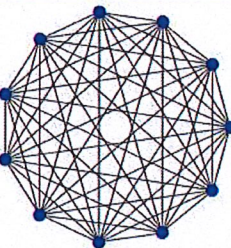
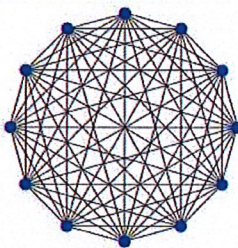
$$E = -\frac{J}{N} \sum_{j < k} s_j s_k - H \sum_{n=1}^N s_n.$$

We normalize the interaction strength by N so that the system retains a finite energy per spin in the $N \rightarrow \infty$ thermodynamic limit.

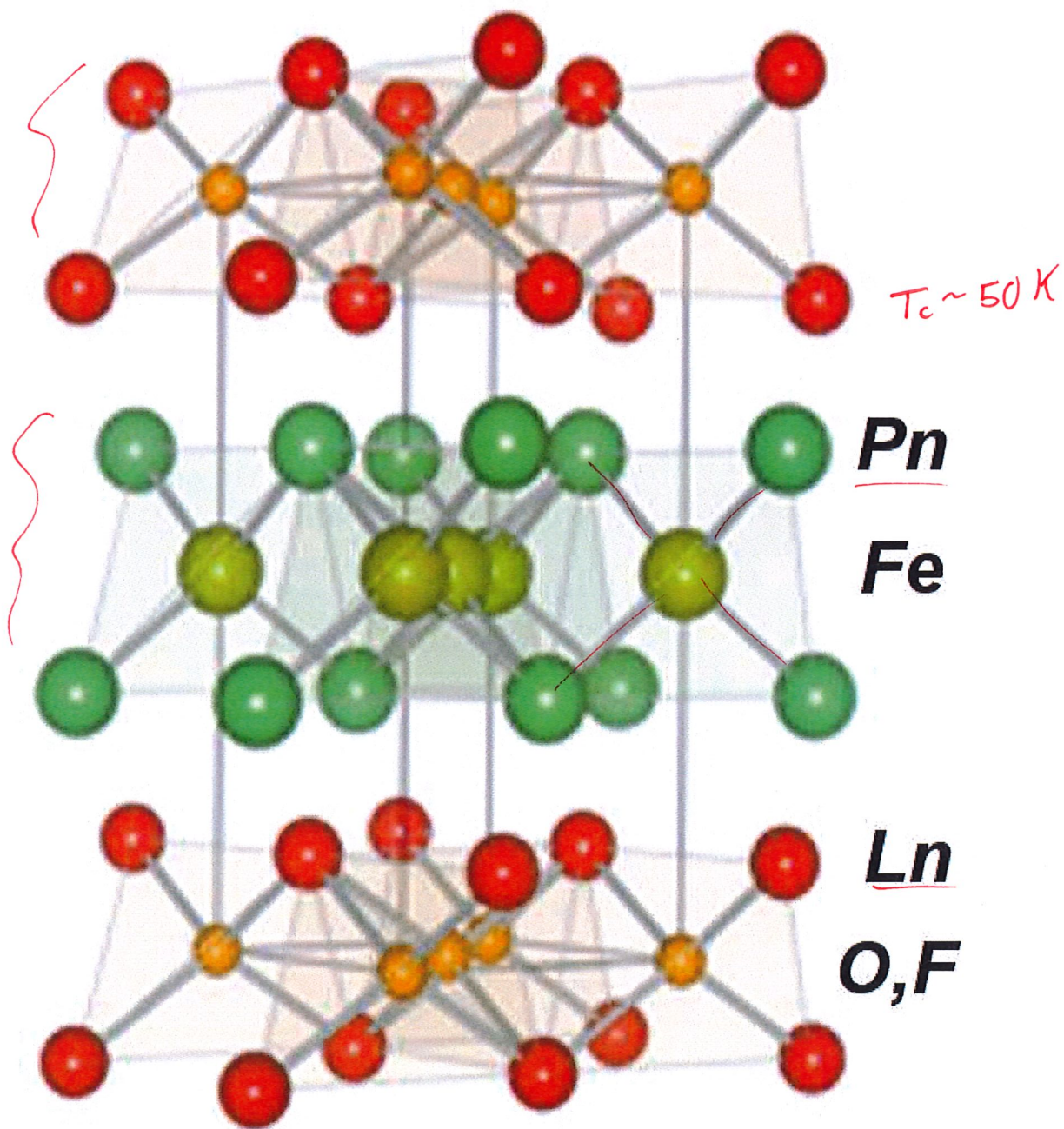
Can you compute a closed-form expression for the partition function of this Ising model on the fully connected lattice? As a hint, it may be profitable to reorganize the calculation into a sum over the $N + 1$ possible values of the magnetization $-1 \leq m \leq 1$, and counting how many micro-states there are with a given magnetization. (This is analogous to the fugacity expansion that reorganizes the

grand-canonical partition function into a sum over possible particle numbers.) The energy above would need to be rewritten in terms of the magnetization, which is easier when summing over all $j < k$ compared to considering only nearest neighbours. Finally, for large N we can approximate the $N + 1$ possible values of m as continuously varying, and integrate

$$Z = \int_{-1}^1 (\dots) dm.$$

$K_1: 0$	$K_2: 1$	$K_3: 3$	$K_4: 6$
			
$K_5: 10$	$K_6: 15$	$K_7: 21$	$K_8: 28$
			
$K_9: 36$	$K_{10}: 45$	$K_{11}: 55$	$K_{12}: 66$
			

en.wikipedia.org/wiki/Complete_graph



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Homework solutions 1

Question 1: Drift and diffusion

Modeling the motion of each oil droplet as a random walk, $10/1000 = 1\%$ of the oil will be in the marine protected area (MPA) when there is a 1% probability of this random walk covering a distance of at least $X = 1$ km. Mathematically, this probability is

$$P = \int_X^\infty p(x) dx = \frac{1}{\sqrt{2\pi t D^2}} \int_X^\infty \exp\left[-\frac{(x - v_{\text{dr}} t)^2}{2t D^2}\right] dx$$

where $P = 0.01$ and we have used the central limit theorem in the form of Eq. 17 in the lecture notes. We need to solve this equation for the time t . We proceed by substituting

$$u = \frac{x - v_{\text{dr}} t}{\sqrt{2t D^2}} \quad du = \frac{dx}{\sqrt{2t D^2}}$$

to find

$$P = \frac{1}{\sqrt{\pi}} \int_U^\infty e^{-u^2} du \quad \text{with} \quad U = \frac{X - v_{\text{dr}} t}{\sqrt{2t D^2}}. \quad (1)$$

The key step is to relate this integral to the gaussian integral and the error function, which are respectively

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty e^{-u^2} du = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-u^2} du = 1;$$
$$\text{erf}(U) = \frac{1}{\sqrt{\pi}} \int_{-U}^U e^{-u^2} du = \frac{2}{\sqrt{\pi}} \int_0^U e^{-u^2} du.$$

We can do this by splitting the $(0, \infty)$ integration domain into two pieces:

$$1 = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-u^2} du = \frac{2}{\sqrt{\pi}} \int_0^U e^{-u^2} du + \frac{2}{\sqrt{\pi}} \int_U^\infty e^{-u^2} du = \text{erf}(U) + 2P.$$

Solving for U , we have $U = \text{erf}^{-1}(1 - 2P) = \text{erf}^{-1}(0.98) \approx 1.64498$, where the numerical value can be obtained using SciPy, as `special.erfinv(0.98)`.

Now all we need to do is solve Eq. 1 for t . Squaring both sides produces the quadratic equation

$$v_{\text{dr}}^2 t^2 - (2X v_{\text{dr}} + 2U^2 D^2)t + X^2 = 0.$$

We are interested in the smaller of the two roots:

$$t = \frac{1}{2v_{\text{dr}}^2} \left[2X v_{\text{dr}} + 2U^2 D^2 - \sqrt{4(X v_{\text{dr}} + U^2 D^2)^2 - 4X^2 v_{\text{dr}}^2} \right]$$
$$= \frac{X v_{\text{dr}} + U^2 D^2 - U D \sqrt{2X v_{\text{dr}} + U^2 D^2}}{v_{\text{dr}}^2}.$$

Plugging in

$$X = 1000 \text{ m} \quad D = 2 \text{ m}/\sqrt{\text{min}} \quad v_{\text{dr}} = 1 \text{ m}/\text{min} \quad U \approx 1.64498,$$

with consistent units, produces $t \approx 863.3$ minutes, a little under 14.4 hours.

Something interesting happens when we now consider how much additional time it will take for the amount of oil inside the MPA to double to 2% of the total. This only changes $P = 0.02$ and $U = \text{erf}^{-1}(1 - 2P) = \text{erf}^{-1}(0.96) \approx 1.45222$, producing $t \approx 878.3$ minutes. That is, while it takes almost fifteen *hours* for the first 10 tonnes of oil to enter the MPA, an additional 10 tonnes enters within another fifteen *minutes*! Once the oil starts arriving the situation rapidly deteriorates, calling for quick action.

Finally, note that the calculation above accounts for the non-zero probability that each oil droplet can randomly walk into the MPA, and then randomly reverse its direction to walk back out again — reducing the amount of oil in the MPA. Such behaviour would not be possible if the droplet were instead ending its random walk by washing onto a shore. That is, the oil would accumulate *more quickly* on a shore compared to an MPA, meaning that it would take *less time* for the same amount of oil to wash up.

Question 2: Negative temperature

In the micro-canonical ensemble, and assuming thermodynamic equilibrium as always in this module, the entropy is $S = \log M(N, E)$, where the fixed energy is $E = n_1 \varepsilon$. The number of micro-states with energy E is

$$M = \binom{N}{n_1} = \frac{N!}{n_1! (N - n_1)!} = \frac{N!}{\frac{E}{\varepsilon} (N - \frac{E}{\varepsilon})!},$$

plugging in $n_1 = \frac{E}{\varepsilon}$. Taking the log and approximating $\log(n!) \approx n \log n - n$ for $n \gg 1$, the constant terms $N - n_1 - (N - n_1)$ all cancel, leaving

$$\begin{aligned} S &\approx N \log N - \frac{E}{\varepsilon} \log \frac{E}{\varepsilon} - \left(N - \frac{E}{\varepsilon}\right) \log \left(N - \frac{E}{\varepsilon}\right) \\ &= N \log \left(\frac{N}{N - \frac{E}{\varepsilon}}\right) + \frac{E}{\varepsilon} \log \left(\frac{N - \frac{E}{\varepsilon}}{\frac{E}{\varepsilon}}\right) \\ &= -N \log \left(1 - \frac{E}{N\varepsilon}\right) + \frac{E}{\varepsilon} \log \left(\frac{N\varepsilon}{E} - 1\right). \end{aligned}$$

Any of the three expressions above is satisfactory. I find it easiest to take the derivative of the third, while the first simplifies standard sanity checks for the entropy: Because we assume $N \gg \frac{E}{\varepsilon}$ and $N \gg (N - \frac{E}{\varepsilon})$, we can see $S > 0$ as it should be. When $\frac{E}{\varepsilon} \rightarrow N$ (so that $n_0 \rightarrow 0$, violating our assumption $n_0 \gg 1$), the first and second terms cancel while the third term vanishes, recovering the trivial limit $S \rightarrow 0$. Similarly, when $\frac{E}{\varepsilon} \rightarrow 0$ (so that $n_1 \rightarrow 0$, violating our assumption $n_1 \gg 1$), the first and third terms cancel while the second term vanishes, recovering the other trivial limit $S \rightarrow 0$.

Moving on to the derivative that provides the temperature, it is

$$\begin{aligned} \frac{1}{T} = \frac{\partial S}{\partial E} &\approx \frac{-N}{1 - \frac{E}{N\varepsilon}} \left(-\frac{1}{N\varepsilon} \right) + \frac{1}{\varepsilon} \log \left(\frac{N\varepsilon}{E} - 1 \right) + \frac{\frac{E}{\varepsilon}}{\frac{N\varepsilon}{E} - 1} \left(-\frac{N\varepsilon}{E^2} \right) \\ &= \frac{N}{N\varepsilon - E} + \frac{1}{\varepsilon} \log \left(\frac{N\varepsilon}{E} - 1 \right) - \frac{N}{N\varepsilon - E} = \frac{1}{\varepsilon} \log \left(\frac{N\varepsilon}{E} - 1 \right). \end{aligned}$$

Inverting, the temperature is

$$T = \frac{\varepsilon}{\log \left(\frac{N\varepsilon}{E} - 1 \right)},$$

and we can see that this is negative when $\frac{N\varepsilon}{E} < 2$, which corresponds to $n_1 = \frac{E}{\varepsilon} > \frac{N}{2}$. As for the non-interacting spin system, this is the 'unnatural' regime in which increasing the amount of energy in the system decreases the number of accessible micro-states and hence the entropy.

Finally, when we consider bringing two such systems into thermal contact with each other, conservation of energy demands

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

as we derived in Section 2.4 of the lecture notes. Supposing $T_A > 0$ while $T_B < 0$, the expression in the parentheses is clearly positive, requiring $\Delta E_A > 0$. In other words, energy flows from the negative-temperature system Ω_B into the positive-temperature system Ω_A . In this way, negative-temperature systems behave as though they are 'hotter' than positive-temperature systems!

Question 3: Heat capacity

There are two terms in the given derivative:

$$c_v = \frac{\partial}{\partial T} \left[\frac{1}{Z} \sum_{i=1}^M E_i e^{-\beta E_i} \right] = - \left(\frac{1}{Z} \frac{\partial Z}{\partial T} \right) \left(\frac{1}{Z} \sum_{i=1}^M E_i e^{-\beta E_i} \right) + \frac{1}{Z} \frac{\partial}{\partial T} \sum_{i=1}^M \underline{E_i} e^{-\beta E_i}.$$

Using the gap on page 48 of the lecture notes, the first term is

$$- \underline{\langle E \rangle} \frac{\partial}{\partial T} \log Z = \langle E \rangle \beta^2 \frac{\partial}{\partial \beta} \log Z = -\beta^2 \langle E \rangle^2.$$

Similarly, the second term is

$$-\beta^2 \frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{i=1}^M E_i e^{-\beta E_i} = \beta^2 \frac{1}{Z} \sum_{i=1}^M E_i^2 e^{-\beta E_i} = \beta^2 \langle E^2 \rangle.$$

Putting them together,

$$c_v = \frac{\langle E^2 \rangle - \langle E \rangle^2}{T^2} = \frac{1}{T^2} \langle (E - \langle E \rangle)^2 \rangle = \beta^2 \underline{\langle (E - \langle E \rangle)^2 \rangle}.$$

$$c_v = \frac{2}{\partial T} \langle (E - \langle E \rangle)^2 \rangle = 0$$

Since the expectation value is a sum over all accessible micro-states,

$$\langle (E - \langle E \rangle)^2 \rangle = \frac{1}{Z} \sum_{i=1}^M (E - \langle E \rangle)_i^2 e^{-\beta E_i} = \sum_{i=1}^M p_i (E_i - \langle E \rangle)^2,$$

we see that the heat capacity is a sum of squares with positive coefficients p_i . Therefore the only way c_v can vanish at finite temperature is if $E_i = \langle E \rangle$ for every accessible micro-state ω_i . That is, the micro-state energies must all be identical, with no fluctuations around the expectation value $\langle E \rangle$, in order for $c_v = 0$.

Building on our work above, it is not too challenging to consider

$$\begin{aligned} \frac{\partial}{\partial T} c_v &= -\beta^2 \frac{\partial}{\partial \beta} c_v = -\beta^2 \frac{\partial}{\partial \beta} [\beta^2 (\langle E^2 \rangle - \langle E \rangle^2)] \\ &= -2\beta^3 (\langle E^2 \rangle - \langle E \rangle^2) - \beta^4 \frac{\partial}{\partial \beta} \left[\frac{1}{Z} \sum_{i=1}^M E_i^2 e^{-\beta E_i} \right] + \beta^4 \frac{\partial}{\partial \beta} \left[\frac{1}{Z} \sum_{i=1}^M E_i e^{-\beta E_i} \right]^2. \end{aligned}$$

For the middle term, we can just repeat our computation above with $E_i \rightarrow E_i^2$:

$$-\beta^4 \frac{\partial}{\partial \beta} \left[\frac{1}{Z} \sum_{i=1}^M E_i^2 e^{-\beta E_i} \right] = \beta^2 \frac{\partial}{\partial T} \left[\frac{1}{Z} \sum_{i=1}^M E_i^2 e^{-\beta E_i} \right] = \beta^4 (\langle E^3 \rangle - \langle E^2 \rangle \langle E \rangle).$$

For the final term, it's easier to consider

$$\beta^4 \frac{\partial}{\partial \beta} \langle E \rangle^2 = 2\beta^4 \langle E \rangle \frac{\partial}{\partial \beta} \langle E \rangle = -2\beta^2 \langle E \rangle \frac{\partial}{\partial T} \langle E \rangle = -2\beta^4 \langle E \rangle (\langle E^2 \rangle - \langle E \rangle^2).$$

Putting these together, and plugging in $c_v = \beta^2 (\langle E^2 \rangle - \langle E \rangle^2)$, we have

$$\frac{\partial}{\partial T} c_v = -2\beta c_v + \beta^4 (\langle E^3 \rangle - 3\langle E^2 \rangle \langle E \rangle + 2\langle E \rangle^3).$$

We can recognize

$$\langle (E - \langle E \rangle)^3 \rangle = \langle E^3 \rangle - 3\langle E^2 \rangle \langle E \rangle + 3\langle E \rangle \langle E \rangle^2 - \langle E \rangle^3 = \langle E^3 \rangle - 3\langle E^2 \rangle \langle E \rangle + 2\langle E \rangle^3,$$

meaning that we have found

$$2c_v + T \frac{\partial}{\partial T} c_v = \frac{\langle (E - \langle E \rangle)^3 \rangle}{T^3}.$$

We can check that the powers of T ensure all three terms in this relation are dimensionless.

Question 4: Indistinguishable spins

From Eq. 39 in the lecture notes, for the internal energy we just need the derivative

$$\begin{aligned}\langle E \rangle_I &= \frac{\partial}{\partial \beta} [\beta F_I] = -NH - \frac{\partial}{\partial \beta} \log [1 - e^{-2(N+1)\beta H}] + \frac{\partial}{\partial \beta} \log [1 - e^{-2\beta H}] \\ &= -NH - \frac{2(N+1)He^{-2(N+1)\beta H}}{1 - e^{-2(N+1)\beta H}} + \frac{2He^{-2\beta H}}{1 - e^{-2\beta H}}.\end{aligned}\quad (2)$$

From the same equation, the entropy is

$$\begin{aligned}S_I &= \beta (\langle E \rangle_I - F_I) \\ &= 2\beta H \left(\frac{e^{-2\beta H}}{1 - e^{-2\beta H}} - \frac{(N+1)e^{-2(N+1)\beta H}}{1 - e^{-2(N+1)\beta H}} \right) + \log \left[\frac{1 - e^{-2(N+1)\beta H}}{1 - e^{-2\beta H}} \right].\end{aligned}$$

These expressions are a bit lengthy, which motivates investigating how they simplify for low and high temperatures.

For **low temperatures** $\beta H \gg 1$, we can define $\varepsilon \equiv e^{-2\beta H} \ll 1$ and write

$$\langle E \rangle_I = -NH - 2(N+1)H\varepsilon^{N+1} \frac{1}{1 - \varepsilon^{N+1}} + 2H\varepsilon \frac{1}{1 - \varepsilon}.$$

The final term is

$$2H\varepsilon \frac{1}{1 - \varepsilon} = 2H\varepsilon + \mathcal{O}(\varepsilon^2),$$

while the middle term is negligible,

$$2(N+1)H\varepsilon^{N+1} \frac{1}{1 - \varepsilon^{N+1}} = \mathcal{O}(\varepsilon^{N+1})$$

with $N \gg 1$. So, overall,

$$\langle E \rangle_I = -NH + 2He^{-2\beta H} + \mathcal{O}(e^{-4\beta H}).\quad (3)$$

In terms of the energy gap $\Delta E = 2H$, this is

$$\langle E \rangle_I = -NH + \Delta E e^{-\beta \Delta E} + \mathcal{O}(e^{-2\beta \Delta E}),$$

where the second term differs by a factor of N compared to $\langle E \rangle_D$ for distinguishable spins at low temperatures.

For the low-temperature entropy, it is again convenient to use the expression $S_I = \beta (\langle E \rangle_I - F_I)$, for which we need the low-temperature expansion of

$$\beta F_I = -N\beta H - \log [1 - \varepsilon^{N+1}] + \log [1 - \varepsilon].$$

The final term is

$$\log [1 - \varepsilon] = -\varepsilon + \mathcal{O}(\varepsilon^2),$$

while the middle term is again negligible,

$$\log [1 - \varepsilon^{N+1}] = \mathcal{O}(\varepsilon^{N+1}),$$

with $N \gg 1$. So for low temperatures

$$\beta F_I = -N\beta H - e^{-2\beta H} + \mathcal{O}(e^{-4\beta H}),$$

and we can check that taking the derivative $\frac{\partial}{\partial \beta} [\beta F_I]$ correctly recovers Eq. 3 for $\langle E \rangle_I$. Putting things together,

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

again differing by factors of N compared to the low-temperature S_D for distinguishable spins.

For **high temperatures** $\beta H \ll 1$, the following expansions for $x \ll 1$ will be useful:

$$\begin{aligned} \frac{1}{1 - e^{-x}} &= \frac{1}{x - \frac{x^2}{2} + \frac{x^3}{6} + \dots} = \frac{1}{x} \left(\frac{1}{1 - \left(\frac{x}{2} - \frac{x^2}{6} + \dots\right)} \right) \\ &= \frac{1}{x} \left[1 + \left(\frac{x}{2} - \frac{x^2}{6}\right) + \left(\frac{x}{2} - \frac{x^2}{6}\right)^2 \right] + \mathcal{O}(x^2) \\ &= \frac{1}{x} \left[1 + \frac{x}{2} + x^2 \left(\frac{1}{4} - \frac{1}{6}\right) \right] + \mathcal{O}(x^2) = \frac{1}{x} + \frac{1}{2} + \frac{x}{12} + \mathcal{O}(x^2) \\ \log[1 - e^{-x}] &= \log \left[x - \frac{x^2}{2} + \frac{x^3}{6} + \dots \right] = \log(x) + \log \left[1 - \left(\frac{x}{2} - \frac{x^2}{6} + \dots\right) \right] \\ &= \log(x) - \left(\frac{x}{2} - \frac{x^2}{6}\right) - \frac{1}{2} \left(\frac{x}{2} - \frac{x^2}{6}\right)^2 + \mathcal{O}(x^3) \\ &= \log(x) - \frac{x}{2} + x^2 \left(\frac{1}{6} - \frac{1}{8}\right) + \mathcal{O}(x^3) = \log(x) - \frac{x}{2} + \frac{x^2}{24} + \mathcal{O}(x^3). \end{aligned}$$

Applying this to the final term in Eq. 2 for $\langle E \rangle_I$, with $x = 2\beta H$,

$$\begin{aligned} \frac{2H e^{-2\beta H}}{1 - e^{-2\beta H}} &= 2H (1 - 2\beta H + 2\beta^2 H^2) \times \left(\frac{1}{2\beta H} + \frac{1}{2} + \frac{\beta H}{6} \right) + \mathcal{O}(\beta^2 H^3) \\ &= \frac{1}{\beta} - H + \frac{\beta H^2}{3} + \mathcal{O}(\beta^2 H^3). \end{aligned}$$

The middle term simply involves replacing every $H \rightarrow H(N+1)$:

$$\frac{2H(N+1)e^{-2\beta H(N+1)}}{1 - e^{-2\beta H(N+1)}} = \frac{1}{\beta} - H(N+1) + \frac{\beta H^2(N+1)^2}{3} + \mathcal{O}(\beta^2 H^3).$$

Subtracting NH from the difference between these two terms produces many cancellations that leave

$$\langle E \rangle_I = \frac{\beta H^2}{3} (1 - (N+1)^2) + \mathcal{O}(\beta^2 H^3) = -\frac{N(N+2)\beta H^2}{3} + \mathcal{O}(\beta^2 H^3). \quad (4)$$

This leading term again differs by factors of N compared to the high-temperature $\langle E \rangle_D$ for distinguishable spins.

Finally addressing the entropy by expanding βF_I , we have

$$\begin{aligned}\log [1 - e^{-2\beta H}] &= \log [2\beta H] - \beta H + \frac{1}{6} (\beta H)^2 + \mathcal{O}([\beta H]^3) \\ \log [1 - e^{-2(N+1)\beta H}] &= \log [2(N+1)\beta H] \\ &\quad - (N+1)\beta H + \frac{1}{6} (N+1)^2 (\beta H)^2 + \mathcal{O}([\beta H]^3).\end{aligned}$$

Again taking the difference and subtracting βNH , all that remains is

$$\beta F_I = -\log(N+1) - \frac{N(N+2)(\beta H)^2}{6} + \mathcal{O}([\beta H]^3).$$

We can again check that taking the derivative $\frac{\partial}{\partial \beta} [\beta F_I]$ correctly recovers Eq. 4 for $\langle E \rangle_I$. Putting things together,

$$S_I = \beta (\langle E \rangle_I - F_I) = \log(N+1) - \frac{N(N+2)(\beta H)^2}{6} + \mathcal{O}([\beta H]^3),$$

significantly different from high-temperature S_D for distinguishable spins.