TWO-STATE PARAMAGNET: NUMERICAL SOLUTION

We can apply the formulas for entropy, temperature and heat capacity to a real-life system by looking at a two-state paramagnet. This is a system of $N$ magnetic dipoles which, when placed in a magnetic field $B$, align themselves so that their magnetic moment $\mu$ points either parallel or antiparallel to the field. The energy of a dipole that is aligned with the field is lower, and we’ll call it $-\mu B$, so that the antiparallel dipole has energy $+\mu B$, and the total energy of the system is

$$U = \mu B (N_\uparrow - N_\downarrow) = \mu B (N - 2N_\uparrow)$$ (1)

where an up arrow indicates parallel alignment and a down arrow antiparallel.

The net magnetization is then

$$M = \mu (N_\uparrow - N_\downarrow) = -\frac{U}{B}$$ (2)

The multiplicity of states is the same as a set of $N$ coins with $N_\uparrow$ heads, so

$$\Omega = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! (N - N_\uparrow)!}$$ (3)

For small systems, we can find the entropy directly as

$$\frac{S}{k} = \ln \Omega$$ (4)

For $N_\uparrow = 98$, we get $U/\mu B = -96$, $M/N\mu = 0.96$, $\Omega = 4950$ and $S/k = 8.507$.

For each value of $N_\uparrow$ from 0 up to $N$, we can evaluate $U$ and $S$ from the formulas above and then plot $S$ versus $U$ (I used Maple for the plot):
For $-100 \leq U/\mu B < 0$, the curve is a 'normal' entropy curve in that the entropy increases with increasing energy, and the curve is concave down. From this we can get the temperature

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$  \hspace{1cm} (5)

Thus the temperature increases with energy in the region $-100 \leq U/\mu B < 0$. At $U = 0$, however, the derivative is zero implying an infinite temperature, and for $U > 0$, the slope is negative, indicating a negative temperature. Since, in this case, negative temperatures occur at higher energies than positive temperatures, we have to interpret a negative temperature as actually being higher than a positive one, in fact, higher than an 'infinite' positive temperature.

In this case, it's probably better to use the entropy of the system as a physical measure of what's going on, since the second law implies that the system will tend to the energy with the greatest entropy, which is $U = 0$. At this energy, there are equal numbers of up and down dipoles, so the system is maximally randomized.

For a system with $N = 100$, we can approximate 5 by taking finite differences. Thus for a given value of $N_\uparrow$ we can estimate the temperature as
\[ T (N^\uparrow) = \frac{\Delta U}{\Delta S} \]
\[ = \frac{U (N^\uparrow + 1) - U (N^\uparrow - 1)}{S (N^\uparrow + 1) - S (N^\uparrow - 1)} \] (6)
\[ = \frac{U (N^\uparrow + 1) - U (N^\uparrow - 1)}{S (N^\uparrow + 1) - S (N^\uparrow - 1)} \] (7)

For \( N^\uparrow = 98 \), we get
\[ T (98) = \frac{U (99) - U (97)}{S (99) - S (97)} = 0.541 \frac{\mu B}{k} \] (8)

This allows us to plot temperature versus energy:

We can see the flip over from \(+\infty\) to \(-\infty\) as the energy increases through zero.

The heat capacity can be obtained similarly as
\[ C = \frac{\Delta U}{\Delta T} \]
\[ = \frac{U (N^\uparrow + 1) - U (N^\uparrow - 1)}{T (N^\uparrow + 1) - T (N^\uparrow - 1)} \] (9)

where we use (7) to calculate the temperatures. For \( N^\uparrow = 98 \) we have

![Graph](image)
The plot of $C$ versus temperature is

![Graph of C versus temperature](image-url)

$C(98) = 0.310Nk$ (11)

[The plot does actually extend down to $T = 0$ if we use the analytic solution, but because we’re dealing with discrete values of $N_\uparrow$, it cuts out early.] This curve is similar in shape to that of an Einstein solid at low temperatures.

Finally, we can plot the magnetization as a function of temperature:
If we start off with $T > 0$ and lower the temperature towards zero, the magnetization gradually increases until at $T = 0$, the system is frozen into the state where all dipoles are parallel to the field. As we increase $T$ to $+\infty$, we approach maximum randomness with equal numbers of dipoles pointing up and down so $M \to 0$. Increasing the temperature beyond $+\infty$ so it becomes negative (starting at $-\infty$) the magnetization again increases, but now the dipoles are aligned antiparallel to the field, eventually saturating as $T \to 0$ from the negative side.

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