TWO-STATE PARAMAGNET - ENTROPY AS A FUNCTION OF TEMPERATURE

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We can use the formulas we obtained for the two-state paramagnet to derive a formula for entropy as a function of temperature. We start with

$$n \equiv \frac{N_{\uparrow}}{N} = \frac{1}{2}\left(1 + \tanh\frac{\mu B}{kT}\right) \tag{1}$$

which gives the fraction n of dipoles, each with magnetic moment μ, aligned parallel to the field B at temperature T. The entropy can be written in terms of n as

$$\frac{S}{k} = -N\left[n \ln n + (1-n)\ln(1-n)\right] \tag{2}$$

From 1 we have

$$1 - n = \frac{1}{2}\left(1 - \tanh\frac{\mu B}{kT}\right) \tag{3}$$

From 2 we have

$$\frac{S}{Nk} = n \ln\frac{1-n}{n} - \ln(1-n) \tag{4}$$

In what follows, we'll define

$$x \equiv \frac{\mu B}{kT} \tag{5}$$

We then have

$$\frac{1-n}{n} = \frac{1-\tanh x}{1+\tanh x} \tag{6}$$

$$= \frac{(1-\tanh x)^2}{1-\tanh^2 x} \tag{7}$$

$$= (1-\tanh x)^2 \cosh^2 x \tag{8}$$

Also

$$1-\tanh x = 1-\frac{e^{x}-e^{-x}}{e^{x}+e^{-x}} \tag{9}$$

$$= 2\frac{e^{-x}}{e^{x}+e^{-x}} \tag{10}$$

$$= \frac{e^{-x}}{\cosh x} \tag{11}$$

$$\ln(1-\tanh x) = -x-\ln(\cosh x) \tag{12}$$

Therefore

$$\frac{S}{Nk} = \frac{1}{2}(1+\tanh x)\ln\left[(1-\tanh x)^{2}\cosh^{2}x\right]+\ln 2-\ln(1-\tanh x) \tag{13}$$

$$= \frac{1}{2}(1+\tanh x)\left[2\ln(1-\tanh x)+2\ln(\cosh x)\right]+\ln 2-\ln(1-\tanh x) \tag{14}$$

$$= (1+\tanh x)\left[-x-\ln(\cosh x)+\ln(\cosh x)\right]+\ln 2+x+\ln(\cosh x) \tag{15}$$

$$= -x(1+\tanh x)+x+\ln(2\cosh x) \tag{16}$$

$$= \ln(2\cosh x)-x\tanh x \tag{17}$$

As $T\to 0$, $x\to\infty$ and

$$\ln(2\cosh x)\to\ln(e^{x}) = x \tag{18}$$

$$x\tanh x\to x\times 1 = x \tag{19}$$

$$\frac{S}{Nk}\to 0 \tag{20}$$

Thus the entropy drops to zero at $T=0$ as required by the third law of thermodynamics.

At the other extreme, when $T\to\pm\infty$, $x\to 0$ and

$$\ln(2\cosh x)\to\ln(2\times 1) = \ln 2 \tag{21}$$

$$x\tanh x\to 0 \tag{22}$$

$$\frac{S}{Nk}\to\ln 2 = 0.693 \tag{23}$$

This is the maximum value of S/Nk which occurs when $n=\frac{1}{2}$ so that half the dipoles are parallel and half are antiparallel.

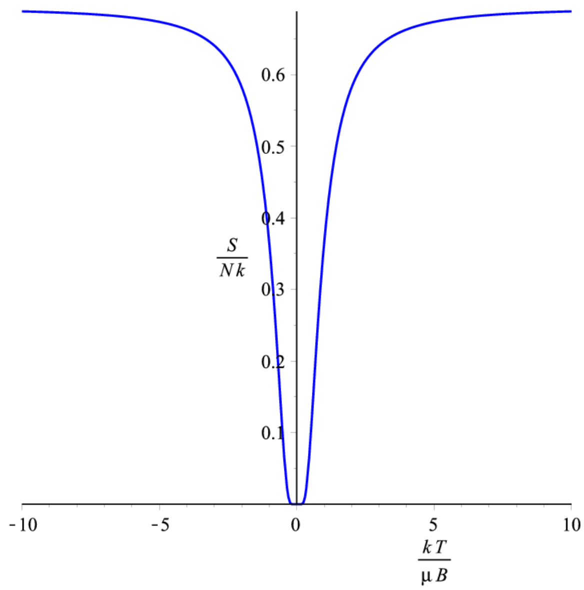

FIGURE 1. Entropy versus temperature.

A plot of S/Nk versus $kT/\mu B$ (effectively a plot of S versus $1/x$) is in Fig. 1.

If we increase B, the dip becomes broader, since a stronger field means that we need a higher temperature to cause significant disruption of the dipoles. Conversely, if we decrease the field, then the dip becomes narrower, since we need very low temperatures to freeze the dipoles into alignment.

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