



6. Systems of weakly interacting constituents

Factorisation of the partition function



- The Boltzmann distribution applies quite generally.
- However the associated partition function, free energy and macro variables like the energy and heat capacity are most easily treated when the particles interact only **weakly** with one another.
- By this we mean that the energy of the r th micro state is $E_r = \epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} + \cdots + \epsilon_{i_N}$ where ϵ_{i_n} is the energy of particle n which is in state i_n
- Eg, in the model magnet, the microstate is given by the states of all N dipoles; the state of dipole n is either the ground state $i_n = 1, \epsilon_1 = -mH$ or the excited state $i_n = 2, \epsilon_1 = +mH$. The total energy is the sum of the individual dipole energies.

Factorisation of the partition function



$$\begin{aligned} Z &= \sum_r \exp(-\beta E_r) = \sum_{i_1 \dots i_N} \exp \left(-\beta \left[\epsilon_{i_1} + \epsilon_{i_2} + \dots + \epsilon_{i_N} \right] \right) \\ &= \left[\sum_{i_1} \exp(-\beta \epsilon_{i_1}) \right] \dots \left[\sum_{i_N} \exp(-\beta \epsilon_{i_N}) \right] \\ &= [Z(1)]^N \end{aligned}$$

where $Z(1)$ is the partition function for a single dipole (easy to calculate)

- Thus we see that the problem of calculating Z for N particles/dipoles is reduced to that of a single particle
- Now $\ln Z = \ln [Z(1)]^N = N \ln Z(1)$
- Hence $F(T) = -kT \ln Z = -NkT \ln Z(1)$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -N \frac{\partial}{\partial \beta} \ln Z(1) = N\bar{e}$$

Factorisation of the partition function



- If we are interested in the state of, say, particle 1, then we can 'sum out' the states of all the other particles 2 to N :

$$\begin{aligned} P_{i_1} &= \sum_{i_2 \cdots i_N} \exp \left(-\beta \left[\epsilon_{i_1} + \epsilon_{i_2} + \cdots + \epsilon_{i_N} \right] \right) \times Z^{-1} \\ &= \frac{\exp(-\beta \epsilon_{i_1}) Z(1)^{N-1}}{Z(1)^N} \\ &= \frac{\exp(-\beta \epsilon_{i_1})}{Z(1)} \end{aligned}$$

- *Key point 13: In a system of N weakly interacting, distinguishable particles, the system partition function is simply $Z = [Z(1)]^N$ and the single particle probability distribution is*

$$P_i = \frac{\exp(-\beta \epsilon_i)}{Z(1)}$$

Model Magnet



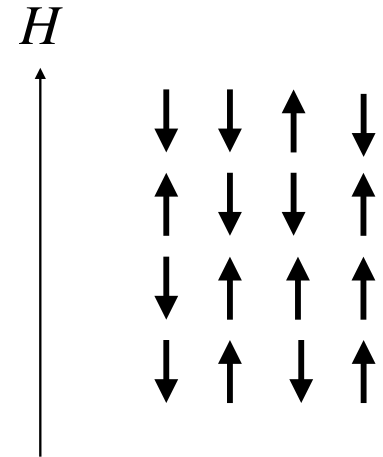
- Recall: single particle partition function for our model magnet

$$Z(1) = 2 \cosh x \quad \text{where} \quad x = \frac{mH}{kT}$$

- Using results from previous section

$$\bar{E} = N\bar{\epsilon} = -N \frac{\partial}{\partial \beta} \ln Z(1) = -NmH \frac{\partial}{\partial x} \ln Z(1) = -NmH \tanh x$$

$$\begin{aligned} S(T) &= k \ln Z + \frac{\bar{E}}{T} \\ &= Nk \ln Z(1) + \frac{N\bar{\epsilon}}{T} \\ &= Nk [\ln(\exp x + \exp -x) - x \tanh x] \end{aligned}$$



Model Magnet



- Define the **magnetisation** as $M = (n_2 - n_1)m$. We have $E = -MH$ and

$$\bar{M} = Nm \tanh x$$

- Low magnetic field: $x = \frac{mH}{kT} \ll 1$ $\tanh(x) \approx x \Rightarrow \bar{M} \approx \frac{Nm^2H}{kT}$
- High magnetic field: $x = \frac{mH}{kT} \gg 1$ $\tanh(x) \approx 1 \Rightarrow \bar{M} \approx Nm$

- Consider too the zero field magnetic susceptibility χ which measures the response of the magnetisation of the system to a small externally applied field

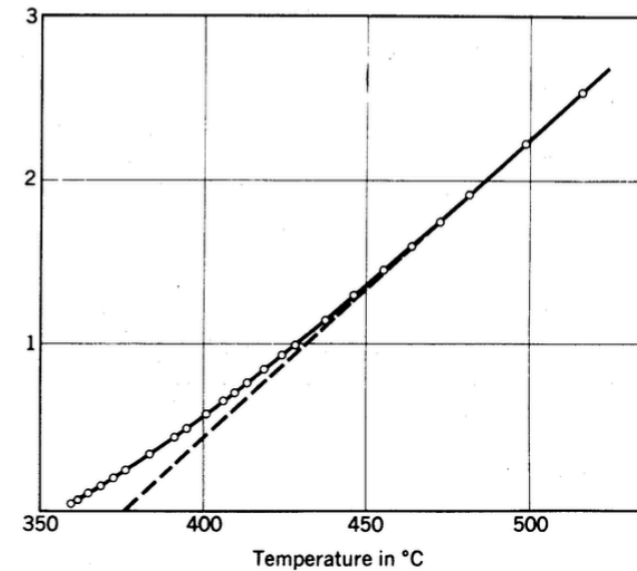
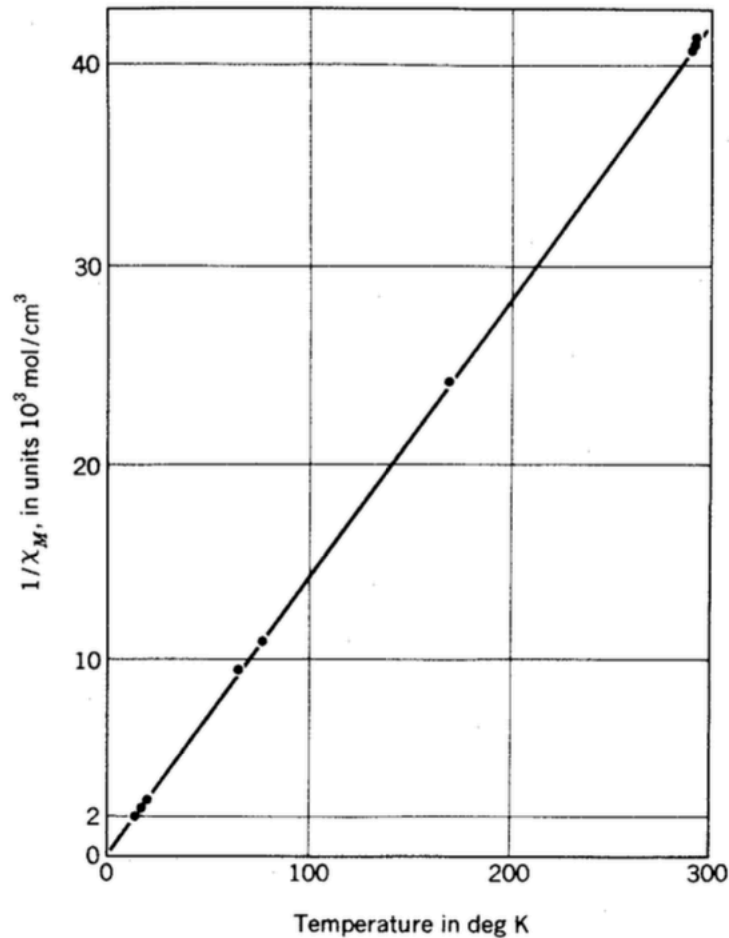
$$\begin{aligned} \chi(H=0) &\equiv \left(\frac{\partial \bar{M}}{\partial H} \right) \bigg|_{H=0} \\ &= \frac{Nm^2}{kT} \end{aligned}$$

$\frac{1}{T}$ dependence is 'Curie law'

Inverse of the magnetic susceptibility for two magnets



Statistical Mechanics



- A salt of gadolinium obeying the Curie law
- Nickel, which shows departures from the Curie law caused by interactions between the dipoles

Model Magnet



- Heat capacity at constant field C_H

$$C_H \equiv \left(\frac{\partial \bar{E}}{\partial T} \right)_H = \left(\frac{\partial x}{\partial T} \right)_H \left(\frac{\partial \bar{E}}{\partial x} \right)_H = N k x^2 \operatorname{sech}^2 x$$

- Low T : $x = \frac{mH}{kT} \gg 1$ $\operatorname{sech}(x) = \frac{2}{\exp(x) + \exp(-x)} \sim 2 \exp(-x) \Rightarrow C_H \rightarrow 0$
- Physical explanation: At $T = 0$ all particles are in the ground state. Have to raise the temperature until $kT \sim 2mH$ (the energy difference to the excited state) before a significant number of dipoles are excited. Thus near $T = 0$, the derivative of internal energy with respect to T is zero.