# 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 $\epsilon_{i_n}$ 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 $i_n = 2, \epsilon_2 = +mH$. The total energy is the sum of the individual dipole energies.

# Factorisation of the partition function



$$Z = \sum_r \exp(-\beta E_r) = \sum_{i_1 \cdots i_N} \exp\left(-\beta\left[\epsilon_{i_1} + \epsilon_{i_2} + \cdots + \epsilon_{i_N}\right]\right)$$

$$= \left[\sum_{i_1} \exp(-\beta\epsilon_{i_1})\right] \cdots \left[\sum_{i_N} \exp(-\beta\epsilon_{i_N})\right]$$

$$= [Z(1)]^N$$

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 $\ln Z = \ln\left[Z(1)\right]^N = N \ln Z(1)$
- Hence $F(T) = -kT\ln Z = -NkT\ln Z(1)$

kp 12

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

# 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*

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

## Basic Hyperbolic Functions

$$\cosh x = \frac{e^x + e^{-x}}{2}, \quad \sinh x = \frac{e^x - e^{-x}}{2}$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}$$

$$\operatorname{sech} x = \frac{1}{\cosh x} = \frac{2}{e^x + e^{-x}}$$

$$\operatorname{cosech} x = \frac{1}{\sinh x} = \frac{2}{e^x - e^{-x}}$$

$$\coth x = \frac{\cosh x}{\sinh x} = \frac{1}{\tanh x} = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

## Some derivatives of hyperbolic functions

$$\frac{d}{dx}(\sinh x) = \cosh x$$

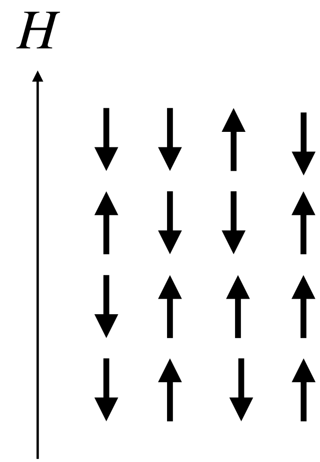
$$\frac{d}{dx}(\cosh x) = \sinh x$$

$$\frac{d}{dx}(\tanh x) = \operatorname{sech}^2 x$$

# Model Magnet

- Recall (chapter 4): single dipole partition function for our model magnet

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




- Using results from chapter 5, mean energy of whole system of $N$ dipoles

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

$$\begin{aligned} S(T) &= k\ln Z + \frac{\overline{E}}{T} \\ &= Nk\ln Z(1) + \frac{N\bar{\epsilon}}{T} \\ &= Nk\left[\ln(2\cosh(x)) - x\tanh x\right] \end{aligned}$$

# Model Magnet



- Important quantity that measures the net total magnetic moment is the **magnetisation:** $M = (n_\uparrow - n_\downarrow)m$.
- This gives total energy $E = -MH$
- But $\overline{E} = NmH\tanh(x)$. Hence $\overline{M} = Nm\tanh x$
- Alternative derivation of magnetisation:

$$
\begin{aligned}
\overline{m} &= \sum_i m_i P_i \\
&= mP(\uparrow) - mP(\downarrow) \\
&= m\left(\frac{e^{\beta mH} - e^{-\beta mH}}{e^{\beta mH} + e^{-\beta mH}}\right) \\
&= m\tanh(\beta mH)
\end{aligned}
$$

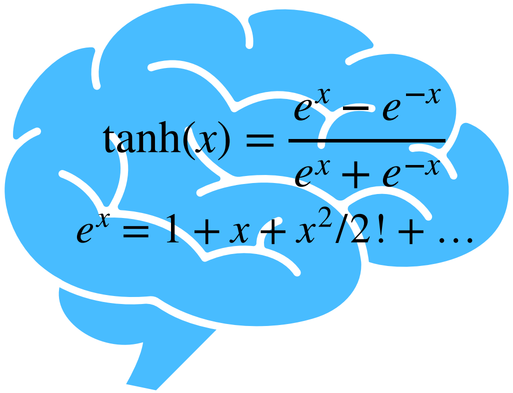
i.e.

$$\overline{M} \equiv N\overline{m} = Nm\tanh(\beta mH) = Nm\tanh x$$

# Model Magnet

- Consider limits of low and high magnetic field

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



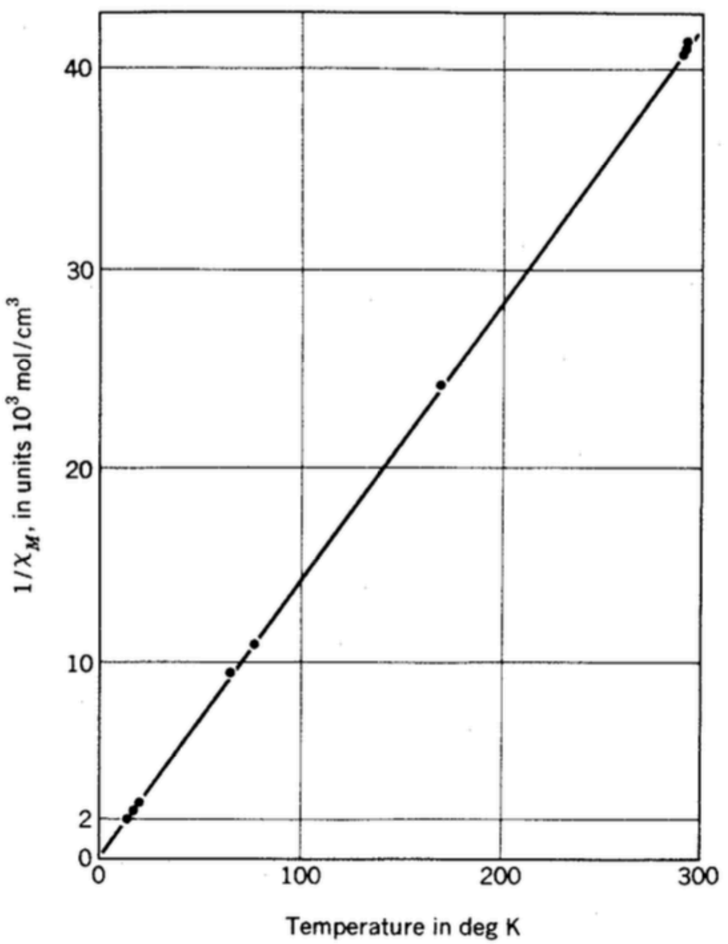

- Consider too the zero field magnetic susceptibility $\chi$ which measures the response of the magnetisation of the system to a small externally applied field (experimentally accessible)

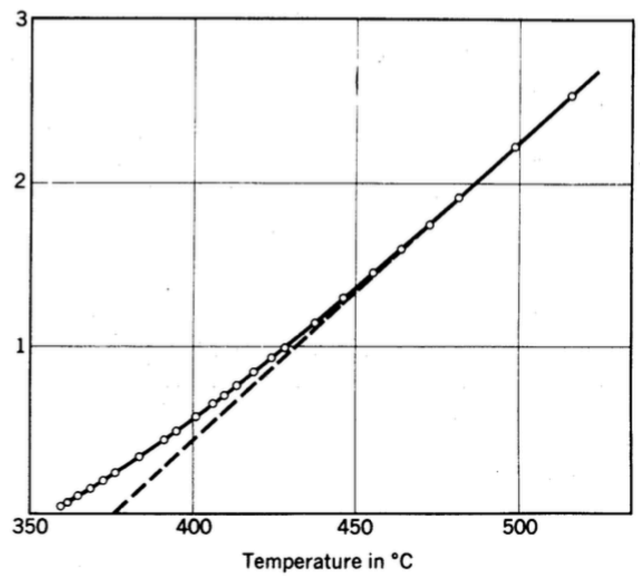
$$\chi(H=0) \equiv \left(\frac{\partial \overline{M}}{\partial H}\right)\Bigg|_{H=0}$$

$$= \frac{Nm^2}{kT}$$

$\dfrac{1}{T}$ dependence is ‘Curie law’

# Inverse of the magnetic susceptibility for two magnets



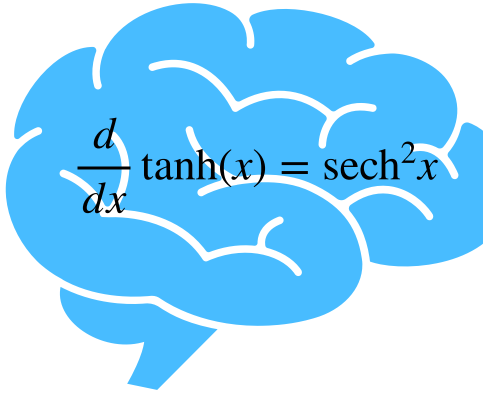

- Nickel, which shows departures from the Curie law caused by interactions between the dipoles

- A salt of gadolinium obeying the Curie law

# Model Magnet

- Heat capacity at constant field $C_H$

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




- Low $T$: $x = \dfrac{mH}{kT} \gg 1$ $\quad \operatorname{sech}(x) = \dfrac{2}{e^x + e^{-x}} \sim 2e^{-x} \Rightarrow C_H \to 0$

- 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.

At end of today’s lecture, please leave the room by **lower exit** (open day activities)