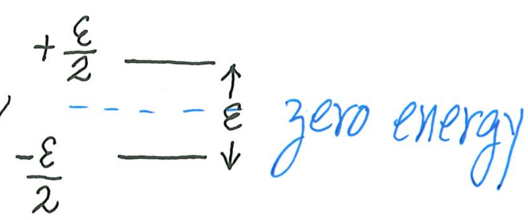
Application A: "Two-level" distinguishable particles and paramagnetism

A. "Two-level" particles

- Each particle has a bounded energy spectrum and there are N distinguishable particles



Stat Mech: the physics of how ε and kT compete

- A physical context

each particle has a magnetic dipole moment $\vec{\mu}$

when a $\vec{B}$-field is applied, there is an interaction energy $(-\vec{\mu}\cdot\vec{B})$

For $\vec{B} = B\hat{z}$ (z-direction)

$$\mathcal{H}_{\substack{\text{interaction}\\ \text{(each particle)}}} = -\mu_z B$$

z-component of magnetic dipole moment
(related to z-component of Angular momentum and charge of electron)

A quantum mechanical result: $\mu_z = -\underset{\substack{\uparrow \\ \text{g-factor}^{+} \\ \text{(depends on } J)}}{g}\,\underset{\substack{\uparrow \\ \text{Bohr magneton} \,\equiv\, \frac{e\hbar}{2m_e}}}{\mu_B}\, m_J$ ← Given J, $m_J = J, J-1, \ldots, -J$

- For $J = 1/2$ (spin-1/2 comes from electron), $g = 2$, $m_J = +1/2, -1/2$ (two values)

$\mu_z = +\mu_B \quad (m_J = -1/2)$, $\mu_z = -\mu_B \quad (m_J = +1/2)$

$$\boxed{\mathcal{H}_{\substack{\text{interaction} \\ \text{(per particle)}}} = \begin{cases} \mu_B B & \text{(when } \mu_z \text{ anti-aligns with } B) \\ -\mu_B B & \text{(when } \mu_z \text{ aligns with } B) \end{cases} \qquad \begin{array}{lcl} +\frac{\varepsilon}{2} & \text{———} & +\mu_B B \\ -\frac{\varepsilon}{2} & \text{———} & -\mu_B B \end{array}}$$

Remark: $\underbrace{J = 1,}_{\text{"3-level"}}$ $\underbrace{J = 3/2,}_{\text{"4-level"}}$ $\underbrace{J = 2,}_{\text{"5-level"}}$ ... cases can be treated similarly
...

+ More general, Landé g-factor when $\vec{J}$ is the total angular momentum with $|\vec{J}|^2 = J(J+1)\hbar^2$

What is a N-particle state?

- Specify for every particle whether it is in the lower or upper energy level

particle : 1, 2, 3, 4, ..., N

lower (l) or upper (u) energy : $\underbrace{u, l, l, u, \ldots, l}$ ← this specifies ONE N-particle state

a string $\{u, l, l, u, \ldots, l\}$

or a string $\{\varepsilon_{u1}, \varepsilon_{l2}, \varepsilon_{l3}, \varepsilon_{u4}, \ldots, \varepsilon_{lN}\}$ specifies one N-particle states

particle 1 in upper energy ε_{u1}

particle 4 in upper energy ε_{u4}

particle N in lower energy ε_{lN}

ε_{u1} –

ε_{l1} –

– ε_{u4}

– ε_{l4}

— ε_{uN}

— ε_{lN}

(possible to have even cases with different energies for different particles (c.f. MRI))

$$\boxed{\text{From } \{l, l, l, \cdots l\} \text{ to } \{u, u, u, \cdots, u\}, \text{ there are } 2^N \text{ strings for } 2^N \text{ N-particle states!}}$$

← All go into calculating Z

What is the energy of a N-particle state?

- Given a N-particle state $\{\varepsilon_{u1}, \varepsilon_{\ell 2}, \varepsilon_{\ell 3}, \varepsilon_{u4}, \cdots, \varepsilon_{\ell N}\}$,

  the Energy of the N-particle state is $E = \varepsilon_{u1} + \varepsilon_{\ell 2} + \varepsilon_{\ell 3} + \varepsilon_{u4} + \cdots + \varepsilon_{\ell N}$

Partition Function Z

$$Z = \sum_{\text{all } 2^N \text{ strings}} e^{-\beta E(\text{string})} = \sum_{\substack{\varepsilon_1 = \varepsilon_{\ell 1},\\ \varepsilon_{u1}}} \sum_{\substack{\varepsilon_2 = \varepsilon_{\ell 2},\\ \varepsilon_{u2}}} \cdots \sum_{\substack{\varepsilon_N = \varepsilon_{\ell N},\\ \varepsilon_{uN}}} e^{-\beta \overbrace{(\varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N)}^{\text{energy of a particular string in the sum}}} \qquad (A1)$$

this is equivalent to summing over all 2^N strings

$$= \sum_{\substack{\varepsilon_1 = \varepsilon_{\ell 1},\\ \varepsilon_{u1}}} \sum_{\substack{\varepsilon_2 = \varepsilon_{\ell 2},\\ \varepsilon_{u2}}} \cdots \sum_{\substack{\varepsilon_N = \varepsilon_{\ell N}\\ \varepsilon_{uN}}} e^{-\beta\varepsilon_1} e^{-\beta\varepsilon_2} \cdots e^{-\beta\varepsilon_N}$$

---

† The point to note here is that we don't need to sort out the number of strings out of 2^N strings for a particular energy, as required by the microcanonical ensemble approach.

$$Z = \underbrace{\left(\sum_{\varepsilon_1=\varepsilon_{\ell 1},\varepsilon_{u1}} e^{-\beta\varepsilon_1}\right)}_{\text{concerns particle \#1}} \cdot \underbrace{\left(\sum_{\varepsilon_2=\varepsilon_{\ell 2},\varepsilon_{u2}} e^{-\beta\varepsilon_2}\right)}_{\text{concerns particle \#2}} \cdots \underbrace{\left(\sum_{\varepsilon_N=\varepsilon_{\ell N},\varepsilon_{uN}} e^{-\beta\varepsilon_N}\right)}_{\text{concerns particle \#N}} \qquad (A2)$$

$$= z_1 \cdot z_2 \cdots z_N$$

(Z of N-particle system factorizes into product of single-particle partition functions†)

$$= \prod_{i=1}^{N} z_i \qquad (A3)$$

product over the N particles

with z_i = partition function of the i^{th} particle

$$= \sum_{\varepsilon_i=\varepsilon_{ui},\varepsilon_{\ell i}} e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon_{ui}} + e^{-\beta\varepsilon_{\ell i}} \qquad \text{(done!)} \qquad (A4)$$

---

† It is interesting to examine why the factorization emerges. We have N independent and distinguishable particles

Back to $\begin{matrix} +\varepsilon/2 \text{ ——— } +\mu_B B \\ -\varepsilon/2 \text{ ——— } -\mu_B B \end{matrix}$ for all N particles

$$Z = z^N \quad , \quad \underbrace{z = e^{-\beta\varepsilon/2} + e^{+\beta\varepsilon/2}}_{} \qquad \text{(A4)}$$

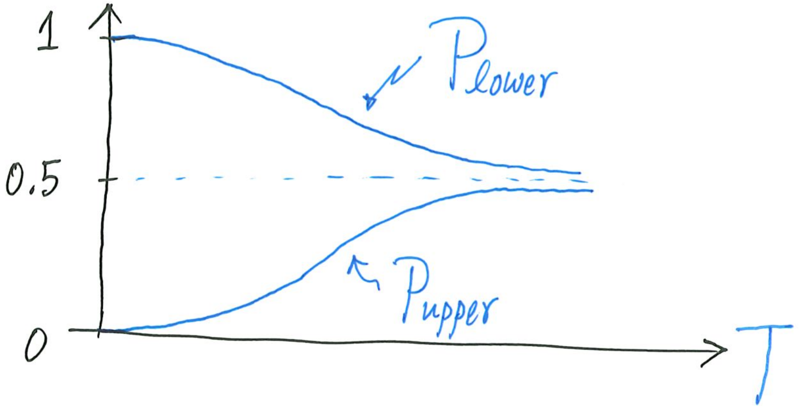
interpretation: $\dfrac{e^{-\beta\varepsilon/2}}{z}$ $\qquad \dfrac{e^{+\beta\varepsilon/2}}{z}$

P_{upper} = prob. of finding a particle in the upper level

prob. of finding a particle in the lower level $= P_{lower}$

$\left[kT \ll \frac{\varepsilon}{2} \Rightarrow z \approx e^{\beta\varepsilon/2}, \text{ so } P_{lower} \approx 1\right]$

(low temp, all particles in lower level, make sense!)



$P_{lower} > P_{upper}$

Temperature alone CANNOT excite more particles to upper level than lower level

Important Stat. Mech. Common Sense.

Mean Energy

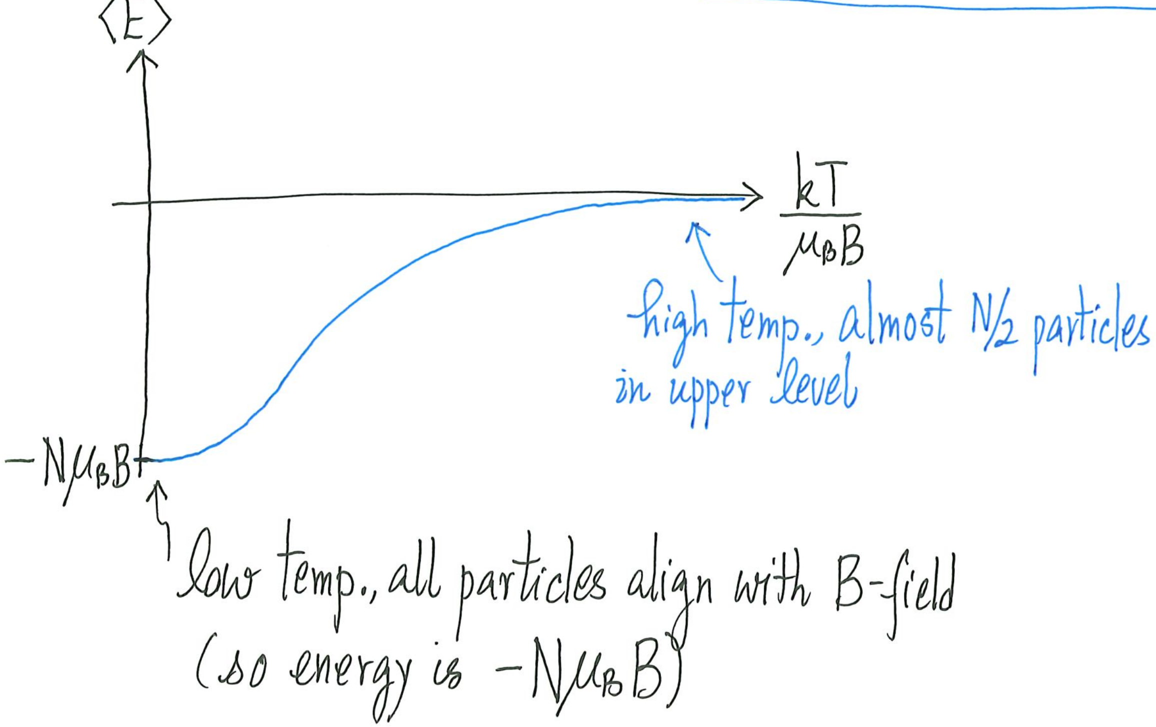
$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = -\underset{\text{extensive (nice)}}{N}\left(\frac{\partial}{\partial\beta}\ln z\right) = -N\frac{\partial}{\partial\beta}\ln\left[e^{\beta\frac{\varepsilon}{2}} + e^{-\beta\frac{\varepsilon}{2}}\right]$$

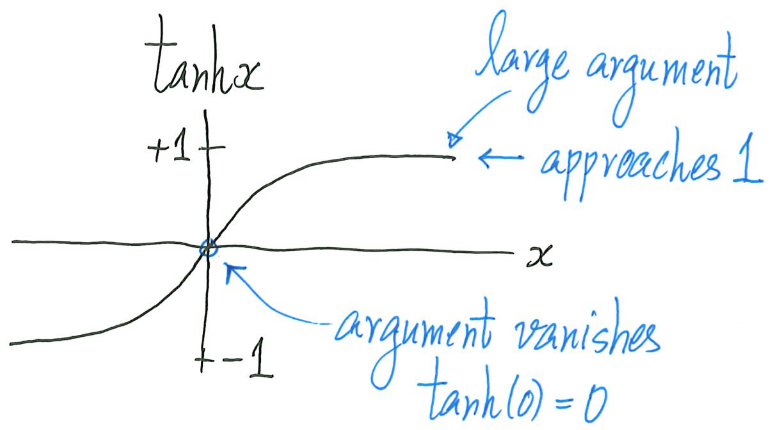
$$= -N\,\frac{\frac{\varepsilon}{2}e^{\beta\varepsilon/2} - \frac{\varepsilon}{2}e^{-\beta\varepsilon/2}}{e^{\beta\varepsilon/2} + e^{-\beta\varepsilon/2}} = -N\frac{\varepsilon}{2}\tanh\left(\frac{\beta\varepsilon}{2}\right)$$

$+\varepsilon/2$ — $+\mu_B B$

$-\frac{\varepsilon}{2}$ — $-\mu_B B$ $\Rightarrow \varepsilon = 2\mu_B B$

$$\therefore \boxed{\langle E\rangle = -N\mu_B B\tanh\left(\frac{\mu_B B}{kT}\right)} \qquad \text{(A5)}$$





Curie Law for Paramagnetic Materials

- Paramagnetic $\Rightarrow$ Magnetization $M \neq 0$ only when $B \neq 0$

[Ferromagnetic $\Rightarrow$ $M \neq 0$ even when $B=0$] (related to dipole moment - dipole moment interaction)

$$\langle E \rangle = -N \mu_B B \tanh\left(\frac{\mu_B B}{kT}\right) = -N \underbrace{\langle \mu_z \rangle}_{\text{stat. mech. mean of } z\text{-component of dipole moment}} B$$

$$\langle \mu_z \rangle = \mu_B \tanh\left(\frac{\mu_B B}{kT}\right) \qquad \text{(A6)}$$

$$\boxed{\begin{array}{c} \mu_B = 5.79 \times 10^{-5}\ \text{eV/Tesla}, \quad B \sim 1\ \text{Tesla} \\ \Rightarrow \mu_B B \sim 10^{-4}\ \text{eV} \\ kT_{room} \sim 1/40\ \text{eV} > \mu_B B \end{array}}$$

$$\underset{\text{(EM)}}{M} = \text{Magnetization} = \frac{\text{Magnetic Dipole Moment}}{\text{Volume}}$$

$$= \frac{N}{V} \mu_B \tanh\left(\frac{\mu_B B}{kT}\right) \approx \frac{N}{V} \mu_B \frac{\mu_B B}{kT} \qquad (\tanh x \approx x, \text{ small } x)$$

$$M = \frac{N}{V}\frac{\mu_B^2}{kT}\mu_0 H \qquad (\because \text{ In EM, } M = \chi H)$$

$$= \chi H$$

with $\chi = \frac{N}{V}\frac{\mu_B^2 \mu_0}{k}\frac{1}{T} \sim \frac{1}{T}$ (A7) Curie's Law observed in experiments

Ex: Find $C(T)$

Ex: Find χ for $J=1$, $J=3/2$, $J=2$, ... $\underbrace{\text{General } J}$

e.g. Cr^{3+} ion

the answer is

$$\chi = \frac{N}{V}\frac{(g\mu_B)^2 \mu_0 J(J+1)}{k}\frac{1}{T} \sim \frac{1}{T} \text{ as well}$$

and $M = \frac{N}{V}(g\mu_B J) B_J\left(\frac{g\mu_B J B}{kT}\right)$

Brillouin function $B_{1/2}(x) = \tanh x$, $B_J(x)$ Complicated!

Remarks

Considered $$H_N = \sum_{i=1}^{N} \mathcal{H}_{\text{interaction}} = \underbrace{\sum_{i=1}^{N} (-\vec{\mu}_i \cdot \vec{B})}_{\text{paramagnetism}}$$

external applied $\vec{B}$-field

(a) Ferromagnetism

Need to consider $\vec{\mu}_i$ interacting with $\vec{\mu}_j$

$$H = \sum_{(i,j)\text{ pairs}} \underbrace{-\mathcal{J}\,\vec{\mu}_i \cdot \vec{\mu}_j}_{} + \sum_{i=1}^{N} (\underbrace{-\vec{\mu}_i \cdot \vec{B}}_{}) \qquad \text{(A8)}$$

energy lowered (-ve sign) when $\vec{\mu}_i$ and $\vec{\mu}_j$ are aligned

effect of an external field

This is the form of the Ising model, XY model, and Heisenberg model of Ferromagnetism.

(b) Evaluate Entropy as a function of T

$F = -kT \ln Z$ and then $S(T)$

$T=0$, $\{l, l, \cdots, l\}$ ← one state

T increases, $S(T) = ?$

(c) Hamiltonian (A8) and result (A6) form the starting point of studying the emergence of spontaneous magnetization (i.e. $B=0$, but $M \neq 0$) in ferromagnetism.