C. Classical Theory of Paramagnetism

- This serves as an example of <u>classical statistical mechanics</u> within the <u>canonical ensemble</u>.

  [c.f. Classical Statistical mechanics examples within microcanonical ensemble such as classical ideal gas and classical oscillators]

- $\nearrow \vec{\mu}$ $\underbrace{\text{ignore quantum features}}$

  no spatial quantization

  $\Rightarrow$ could point to any direction

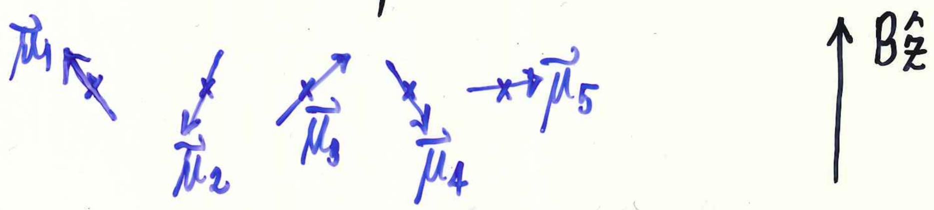
$$Z = \sum_{\substack{\text{all N-particle}\\ \text{states } i}} e^{-\beta E_i} \quad \text{(definition)}$$

$\left\{ \begin{array}{l} \text{What to "sum" over?} \\ \text{What are } E_i \text{?} \end{array} \right.$

C. Classical Theory of Paramagnetism +

(Langevin 1905)

- N classical magnetic dipoles, localized (hence distinguishable), non-interacting dipoles in a uniform field $\vec{B} = B\hat{z}$
- Classical dipoles

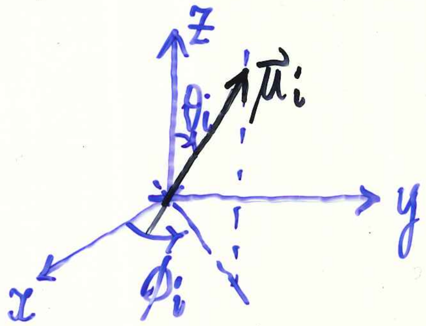


$\mu = |\vec{\mu}_i|$ (for all i)

$\vec{\mu}_i$: can be of <u>any orientation</u> relative to $\hat{z}$-axis

(Quantum: μ_z is quantized)

- Each dipole's state is specified by (θ, ϕ)



(θ_i, ϕ_i): i^{th} dipole

continuous variables

Interaction energy of i^{th} dipole with $\vec{B} = B\hat{z}$

$$= -\vec{\mu}_i \cdot \vec{B} = -\mu B \cos\theta_i$$

[(θ_i, ϕ_i) form the phase space of i^{th} dipole]

+ This also serves as an example of classical stat. mech. (see later chapter).

- Non-interacting dipoles:

Total interaction energy (hence Hamiltonian of this problem)

$$E = E(\theta_1,\phi_1,\theta_2,\phi_2,\cdots,\theta_N,\phi_N) = \sum_{i=1}^{N} -\mu B\cos\theta_i$$

[non-interacting, no dipole-dipole interaction term]

- $$\sum_{\text{states } i} e^{-\beta E_i} = Z$$

  - A state of the N-dipole system is specified by a set of values $\underbrace{(\theta_1,\phi_1,\theta_2,\phi_2,\cdots,\theta_N,\phi_N)}_{\text{all continuous variables}}$

  - $\sum_{\text{states } i} \longrightarrow$ integrate over all θ_i,ϕ_i

$$\int d\Omega_1 \int d\Omega_2 \cdots \int d\Omega_N$$

integrate over phase space

"solid angles"

where $\int d\Omega_1 = \int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \sin\theta_1$

N-dipole partition function

$$Z = \int\cdots\int d\Omega_1 d\Omega_2 \cdots d\Omega_N\, e^{\beta\mu B\sum_{i=1}^{N}\cos\theta_i}$$

"looks complicated?"

(classical approach)

- Since there is no interaction between dipoles, there is no term in E that involves (e.g. $\cos(\theta_i-\theta_j)$), this feature leads to factorization of Z

$$Z = z_1\cdot z_2\cdots z_N = (z_1)^N$$

where

$$z_1 \equiv \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu B\cos\theta} \qquad (d\Omega = \sin\theta d\theta d\phi)$$

one-particle partition function

$$= 2\pi \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu B\cos\theta} \qquad (x \equiv \cos\theta)$$

$$= 2\pi \int_{-1}^{1} dx\, e^{\beta\mu B x} = \frac{2\pi}{\beta\mu B}\left(e^{\beta\mu B} - e^{-\beta\mu B}\right)$$

$$= \frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)$$

as expected we see $\frac{\mu B}{kT} \to \frac{\text{magnetic energy}}{\text{thermal energy}}$

$$\therefore\ F = -\frac{N}{\beta}\ln z = -NkT\ln z$$

$$M = \frac{1}{V}\left(\frac{-\partial F}{\partial B}\right) = \frac{N}{V}\frac{1}{\beta}\left[\frac{\partial}{\partial B}\ln\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right)\right]$$

$$= \frac{\mathcal{N}}{\beta}\frac{\partial}{\partial B}(\beta\mu B)\frac{d}{dy}\left[\ln\left(\frac{4\pi}{y}\sinh y\right)\right] \qquad (\text{put } y = \beta\mu B)$$

$$= \mathcal{N}\mu\left(\coth y - \frac{1}{y}\right)$$

$$\equiv \underbrace{\mathcal{N}\mu}_{\text{saturate magnetisation}} L(y)$$

$L(y)$ = Langevin function $= \coth y - \frac{1}{y}$

(i) When $y = \frac{\mu B}{kT} \gg 1$ (high field / low T)

$$L(y) \approx 1 \Rightarrow M = \mathcal{N}\mu \quad \text{(saturation)}$$

(all dipoles aligned with field)

(ii) When $y = \frac{\mu B}{kT} \ll 1$ (low field / high T)

$$\coth y = \frac{e^y + e^{-y}}{e^y - e^{-y}} \simeq \frac{1 + \frac{y^2}{2!} + \frac{y^4}{4!}}{y + \frac{y^3}{3!} + \frac{y^5}{5!}} \approx \frac{1}{y}\left(1 + \frac{y^2}{3}\right) \quad [y \ll 1]$$

$$\therefore L(y) \approx \frac{1}{y}\left(1 + \frac{y^2}{3}\right) - \frac{1}{y} = \frac{y}{3} \qquad (y \ll 1)$$

$$\therefore M = \mathcal{N}\mu \frac{y}{3} = \frac{\mathcal{N}\mu^2 B}{3kT} = \underbrace{\frac{\mathcal{N}\mu^2\mu_0}{3kT}}_{\chi} H$$

$$\chi = \frac{\mathcal{N}\mu^2\mu_0}{3k} \cdot \frac{1}{T} \qquad \text{(Curie's law)}$$

Things to note:

- Non-interacting: $Z = z_1 \cdot z_2 \cdots z_N$ (both classical and quantum)
- $\sum_{\text{states } i} \rightarrow$ integrate over continuous variables

$$\int \cdots \int d\Omega_1 \cdots d\Omega_N$$

$\hookrightarrow$ integrate over phase space

Remarks:

- With non-interacting moments, we can only obtain paramagnetic behaviour.
- To have ferromagnetic behaviour, i.e., $M \neq 0$ even when $B = 0$ at $T < T_c$, we need to include interactions between magnetic moments.
- The idea is that if a moment "wants" its neighbouring moments to be aligned in its direction, then even a short-range (e.g. nearest-neighbour) interaction may lead to long-range ordering (e.g. ferromagnetism) when interaction energy wins over thermal effect.

E.g.,

$$H = \sum_{\{\text{nearest neighboring pairs}\}} -J\,\vec{\mu}_i \cdot \vec{\mu}_j$$

is a standard Hamiltonian for studying ferromagnetism.