Paramagnetism

- Apply magnetic field → gives Magnetization
- $\chi \sim \frac{1}{T}$ (χ = magnetic susceptibility) (a tiny effect)
- An application of two-level systems ($J=\frac{1}{2}$ case)
- Magnetic moments with discrete $\hat{z}$-components

  $J=\frac{1}{2} \Rightarrow m_J = \begin{cases} +\frac{1}{2} \\ -\frac{1}{2} \end{cases} \Rightarrow$ two-level system
- General $J \Rightarrow m_J = \underbrace{J, J-1, \ldots, -J}_{2J+1 \text{ values}}$

  $\Rightarrow$ "$2J+1$"-level system (bounded single-particle energy spectrum)

  Also gives $\chi \sim \frac{1}{T}$ (Curie's law)
- Even ignoring discrete $\hat{z}$-component

  $\Rightarrow$ classical magnetic moments

  $\Rightarrow$ classical statistical mechanics

  Also gives $\chi \sim \frac{1}{T}$

$\chi \sim \frac{1}{T}$ experimentally observed for paramagnetic materials

B. Paramagnetism in Solids

[Warning: The study of magnetic properties of solids is often complicated by (i) choice of units (SI or cgs) [cgs is often used in research], (ii) $\vec{B}$ vs $\vec{H}$ fields, and (iii) the proper form of magnetic energy term in various thermodynamic potentials]

- Here, our discussion will focus on getting the experimentally observed feature.

Solids[†] → paramagnetic ($H \neq 0 \Rightarrow M \neq 0$) [Magnetization]

→ ferromagnetic ($\underbrace{H=0,\ M\neq 0}_{\text{"spontaneous magnetization"}}$ under suitable conditions)

- Here, we consider paramagnetism.

[†] In fact, every material has also a diamagnetic response, which is usually small compared with paramagnetic and ferromagnetic responses.

Magnetic Susceptibility, χ

[Warning: There are different ways of defining χ in different books, even all using SI units!]

The magnetic effects of a material is quantified by†:

$$\vec{M} = \chi \vec{H} \leftarrow \text{"magnetic field intensity" (Units: } A\,m^{-1})$$

$\vec{M}$: magnetization

↳ Meaning: Magnetic dipole moment per unit volume (Units: $\frac{A \cdot m^2}{m^3} = A\,m^{-1}$)

χ: dimensionless (magnetic susceptibility)

- Paramagnetic: $\chi > 0$ but $\chi \ll 1$

  Typical values: $\chi \sim 10^{-5} - 10^{-4}$ for paramagnetic materials

  $CuSO_4$: $\chi \sim 3.8 \times 10^{-4}$ at $T = 300K$

  AND $\chi \sim \frac{1}{T}$ (Curie's law)

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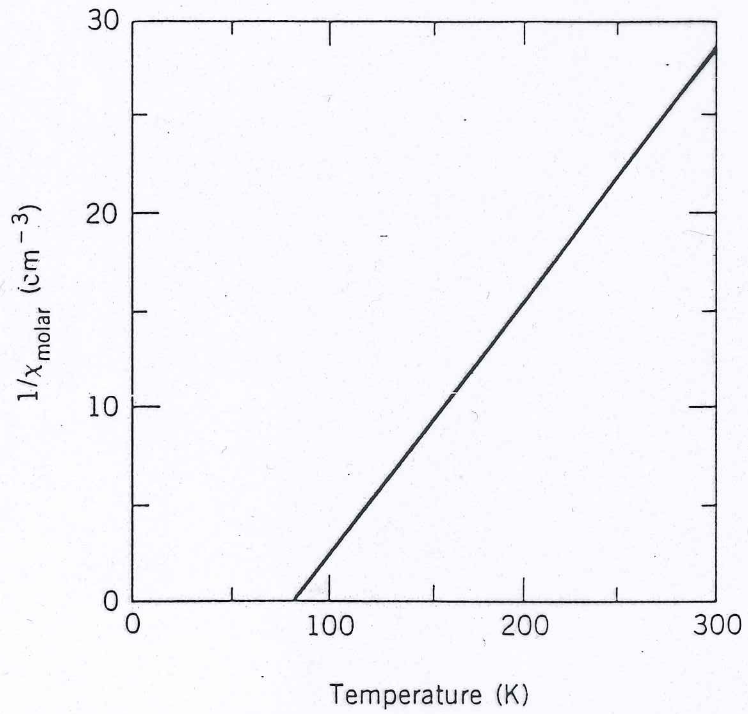
† This is a popular definition. Another definition is $\vec{M} = \chi \frac{\vec{B}}{\mu_0}$. As long as $\chi \ll 1$, there is not much difference.

Exp'tal fact

Curie's Law

$$\chi \sim \frac{1}{T} \quad \text{high temperature}$$

χ = susceptibility



EuO

The reciprocal of the molar susceptibility (in Gaussian units) as a function of temperature for EuO. The line represents theoretical values for noninteracting ions in states with $L' = 0$ and $S' = \frac{7}{2}$, while the dots represent experimental values. The linearity of the plot attests to the validity of the Curie law.

We want to explain this exp'tal fact using stat. mech.

Note: The molar susceptibility χ_{molar} is related to the magnetic dipole moment per mole of the substance and its SI unit is formally $m^3\,\underbrace{mol^{-1}}_{\text{actually no dimension}}$ (thus m^3)

Given in handbooks

$$\chi_{molar} = \chi \cdot V_m \leftarrow \text{molar volume}$$

χ_{molar} Units: $m^3\,mol^{-1}$; χ: dimensionless

Paramagnetism χ is +ve but $\chi \ll 1$ (tiny effect)[†]

Free space: $\vec{B}$ and $\vec{H}$ are related by

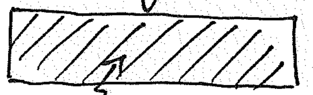
$$\vec{B} = \mu_0 \vec{H}$$

$\vec{B}$: Magnetic induction

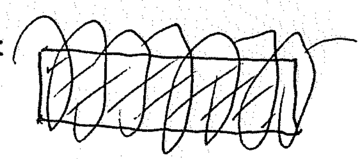
μ_0: permeability of vacuum

$\vec{H}$: magnetic field intensity (due to some source (e.g. current) outside)

Matter:



e.g.



$\vec{B} = ?$ in presence of $\vec{H}$

$$\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M}$$

$\mu_0 \vec{M}$: material's response enters

$\vec{B}$ is altered by presence of material

$$\vec{B} = \mu_0(\vec{H}+\vec{M}) = \mu_0(\vec{H}+\chi\vec{H}) = \mu_0(1+\chi)\vec{H}$$
$$\equiv \mu_0 \mu_r \vec{H} \equiv \mu \vec{H}$$

$$\mu_r = 1 + \chi$$

μ_r: relative permeability

χ: magnetic susceptibility

Paramagnetic Materials: $\chi \ll 1$

$$\Rightarrow \mu_r \approx 1 \quad \text{OR} \quad \mu \approx \mu_0$$

† This page is about EM theory.

Essential Quantum Physics Background

- Atom/ion $\Leftrightarrow$ tiny magnet

$$\vec{\mu} = g\left(\frac{-e}{2m}\right)\vec{J}$$

$\vec{\mu}$: Magnetic moment

g: Landé g-factor — a number of $O(1)$ that depends on L, S, J

m: electron mass

$\vec{J}$: total angular momentum, $\vec{J} = \vec{L} + \vec{S}$

OR
$$\boxed{\vec{\mu} = -g\left(\frac{e\hbar}{2m}\right)\frac{1}{\hbar}\vec{J} = -g\frac{\mu_B}{\hbar}\vec{J}} \quad (1)$$

with $\mu_B \equiv \dfrac{e\hbar}{2m}$ = Bohr magneton $= 9.27\times10^{-24}$ J/Tesla (or $A\cdot m^2$)

$= 5.79\times10^{-5}$ eV/Tesla — set energy scale of problem

Given quantum number J,

$|\vec{J}| = \sqrt{J(J+1)}\,\hbar$; $J_z = m_J \hbar$ ("$\hat{z}$-component")

with $m_J = \underbrace{J, J-1, \ldots, -J}_{(2J+1)\text{ values}}$

Hints: The quantum story here follows the flow: Orbital angular momentum, Spin angular momentum, multi-electron atoms/ions, Spin-orbit coupling, total angular momentum, magnetic moments and angular momentum, Hund's rules for getting S, L, J, g-factor, Zeeman effect.

What is the "$\hat{z}$-direction"?

- No direction is special without an applied $\vec{B}$-field
- Presence of $\vec{B}$-field, there is a special direction!
  Call it $\hat{z}$, i.e. $\vec{B} = B\hat{z}$

$\vec{\mu}$ (magnetic moment) interacts with $\vec{B}$

$$\boxed{\underset{\substack{\uparrow\\ \text{interaction energy}}}{\mathcal{E}} = -\vec{\mu}\cdot\vec{B}} \quad (2)$$

"$-$" sign $\Rightarrow$ $\vec{\mu}$ aligns with $\vec{B}$ (lower energy)
$\vec{\mu}$ anti-aligns with $\vec{B}$ (higher energy).

$\Rightarrow$ single moment/particle Hamiltonian h

Eqs. (1) and (2) $\Rightarrow$ Zeeman Effect

$$\mathcal{E} = -\vec{\mu}\cdot\vec{B} = -\mu_z B = -\left(-g\frac{\mu_B}{\hbar}\right)B\overset{m_J\hbar}{\widetilde{J_z}}$$

$$\Rightarrow \boxed{\mathcal{E} = g\mu_B B\, m_J} \quad \text{depends on } m_J$$

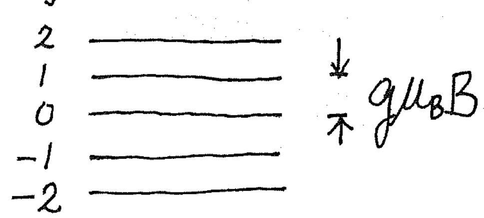
e.g. $J=2$

$B=0$

5-fold degenerate ($m_J = 2, 1, 0, -1, -2$)

($2J+1$) states are degenerate

$B\neq0$

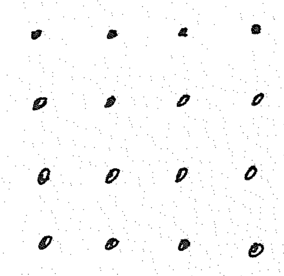


evenly spaced & bounded

$B\neq0$ lifts degeneracy

(a) <u>Understanding the Curie's law: $J=\frac{1}{2}$ case</u>

- Solids



Array of atoms
$\Rightarrow$ array of magnetic moments

<u>Paramagnetism</u>

- $M \neq 0$ only when there is an applied field
- $M = \chi H$ and $\chi \ll 1$ ($\sim 10^{-5}$) (tiny response)

<u>Implications</u> (or Approximations)

- Magnetic moments are independent
  - ignore $\vec{\mu}_i$ influence[+] on $\vec{\mu}_j$
    ($-\vec{\mu}\cdot\vec{B}$ more important)

$\Rightarrow$ $\boxed{\text{Array of independent magnetic moments, each interacting with an external applied field}}$

Physical Model of Paramagnetism

[+] In EM theory, $\vec{\mu}_i$ interacts with $\vec{\mu}_j$. This is weak based on EM equation of dipole-dipole interaction. However, Quantum Effect could lead to a stronger interaction giving rise to <u>ferromagnetism</u>.

$J=\frac{1}{2}$ case

- Meaning: $\underbrace{L=0,\ S=\frac{1}{2}}_{g=2}$ $\Rightarrow$ Entirely due to spin-half

$g=2$ [Recall: $\vec{\mu}_S = -\frac{e}{m}\vec{S} = 2\left(\frac{-e}{2m}\right)\vec{S}$]

due to spin — thus $g=2$

$$\therefore\ \boxed{\mathcal{E} = g\mu_B B m_J = \begin{cases} \mu_B B & (m_J=\frac{1}{2}) \\ -\mu_B B & (m_J=-\frac{1}{2}) \end{cases}}$$

$\mu_B \sim 10^{-5}\,\frac{\text{eV}}{\text{Tesla}}$

$B \sim$ Tesla

Just a two-level system!

$B=0$		$B\neq 0$	
	$\boxed{m_J}$	$\boxed{\mathcal{E}}$	
2-fold degenerate	$+\frac{1}{2}$	$\mu_B B$	moment anti-aligned (spin aligned)
	$-\frac{1}{2}$	$-\mu_B B$	moment aligned (spin anti-aligned)

compared with (Sec. A): $+\frac{\varepsilon}{2}$, $-\frac{\varepsilon}{2}$, gap ε

$\boxed{\text{"}\varepsilon\text{" in Sec. A} = 2\mu_B B = g\mu_B B}$

$$\boxed{\begin{aligned} Z &= z^N \quad \text{(independent, distinguishable)} \\ z &= \sum_{\mathcal{E}=\mathcal{E}_\ell,\mathcal{E}_u} e^{-\beta\mathcal{E}} = e^{-\beta\mu_B B} + e^{\beta\mu_B B} \end{aligned}}$$

From here, either use physical reasoning or plug formulas. And the same physics emerges, of course.

Physical Reasoning

M = Magnetization = $\frac{\text{Magnetic Moment}}{\text{Volume}}$ (by definition)

$= \mathcal{N}\langle\mu_z\rangle$

$\mathcal{N}$: # ions/atoms per unit volume $\leftarrow \frac{N}{V}$

$\langle\mu_z\rangle$ = Average value of $\hat{z}$-component of one ion/atom in the presence of B

For $\vec{B}=B\hat{z}$,

m_J	μ_z	$\mathcal{E}$	Prob. of finding ion/atom	
$+\frac{1}{2}$	$-\mu_B$ (anti-align)	$+\mu_B B$	$\frac{1}{z}e^{-\beta\mu_B B}$	(smaller)
$-\frac{1}{2}$	$+\mu_B$ (align)	$-\mu_B B$	$\frac{1}{z}e^{\beta\mu_B B}$	(bigger)

$$\langle\mu_z\rangle = \underbrace{(+\mu_B)\cdot\frac{1}{z}e^{\beta\mu_B B}}_{\text{align}} + \underbrace{(-\mu_B)\cdot\frac{1}{z}e^{-\beta\mu_B B}}_{\text{anti-align}} \qquad (*)$$

$$= \mu_B\,\frac{e^{\beta\mu_B B} - e^{-\beta\mu_B B}}{e^{\beta\mu_B B} + e^{-\beta\mu_B B}} = \mu_B \tanh(\beta\mu_B B)$$

$$= \mu_B \tanh\left(\frac{\mu_B B}{kT}\right) = \frac{g\mu_B}{2}\tanh\left(\frac{g\mu_B B}{2kT}\right) \quad (g=2)$$

$$\therefore\ \boxed{M = \mathcal{N}\mu_B \tanh\left(\frac{\mu_B B}{kT}\right)} = \mathcal{N}\frac{g\mu_B}{2}\tanh\left(\frac{g\mu_B B}{2kT}\right)$$

Key result

Plug Formula

- What is the formula to plug?

$$z = e^{-\beta\mu_B B} + e^{\beta\mu_B B}$$

How to get $\langle\mu_z\rangle$? (as in Eq. (*))

$$\langle\mu_z\rangle = \frac{1}{z}\frac{1}{\beta}\left(\frac{\partial z}{\partial B}\right)_\beta \qquad \text{(Check) (Ex.)}$$

$$= \left(\frac{\partial}{\partial B} kT \ln z\right)_T = \left(-\frac{\partial}{\partial B}(-kT\ln z)\right)_T$$

For N magnetic moments in a volume V,

$$F = -kT\ln Z = -NkT\ln z \qquad (\because Z = z^N)$$

$$\text{Total Magnetic Moment in Volume } V = \left(-\frac{\partial F}{\partial B}\right)_T$$

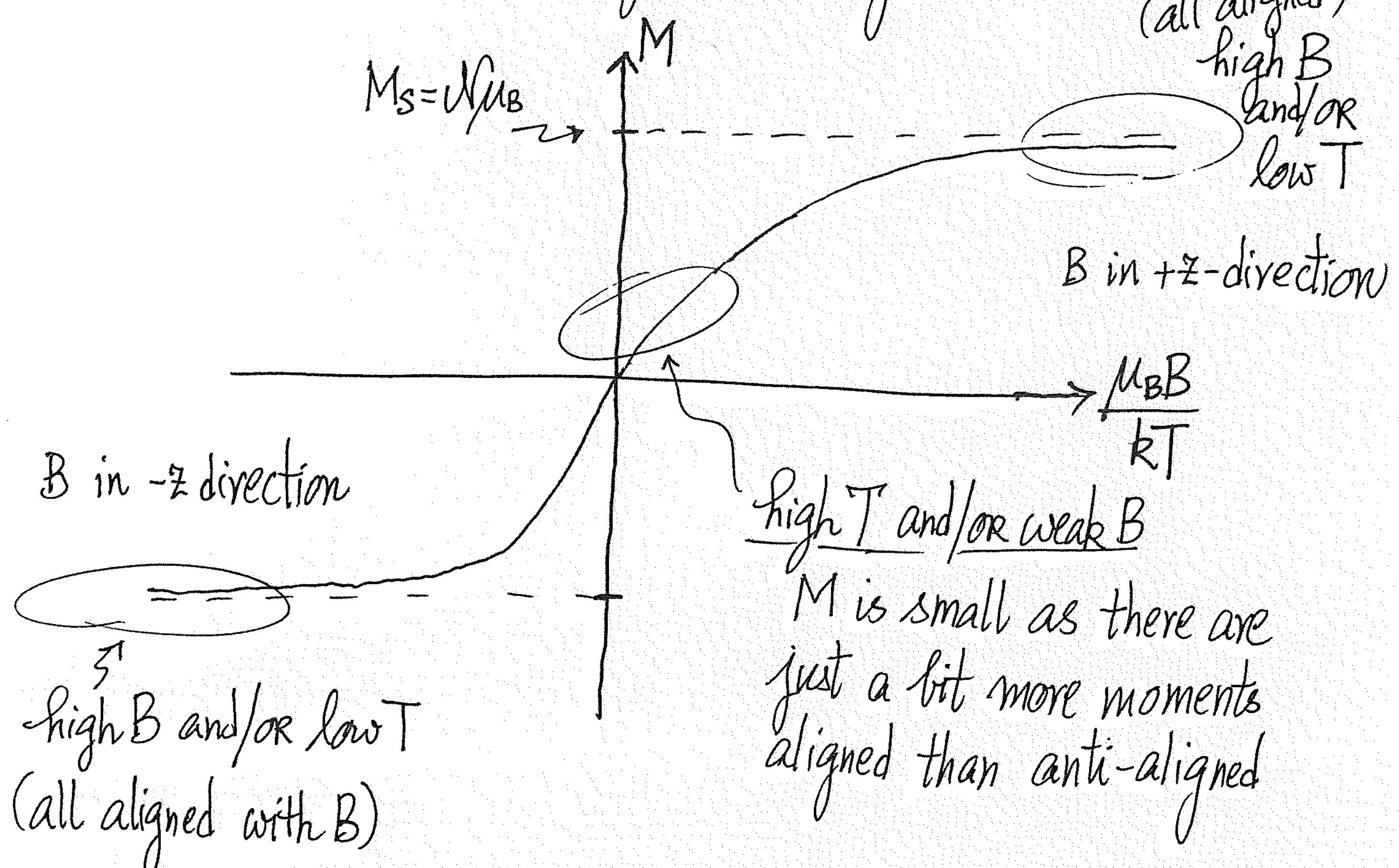
$$\boxed{\text{Magnetization } M = -\frac{1}{V}\left(\frac{\partial F}{\partial B}\right)_T} = \frac{N}{V}\langle\mu_z\rangle = \mathcal{N}\langle\mu_z\rangle$$

- Formula to get M
- Work for other values of J
- Physical argument led us to a formula

$$M = \mathcal{N}\langle\mu_z\rangle = \underbrace{\mathcal{N}\mu_B}_{M_s} \tanh\left(\frac{\mu_B B}{kT}\right) \qquad (J = 1/2)$$

M_s: saturation magnetization (all aligned) [as big as M can be]

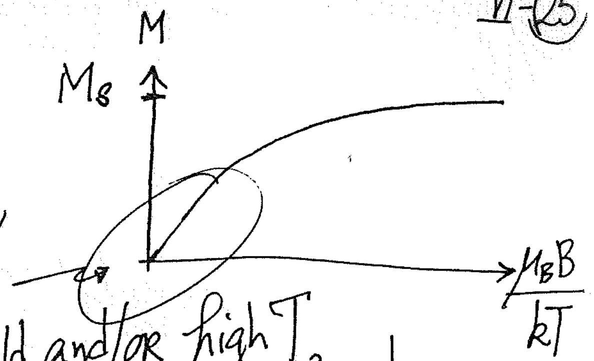
$\frac{\mu_B B}{kT}$: interaction energy competes with thermal energy



Similar behavior of M/M_s vs $\frac{g\mu_B B}{2kT}$ is found/observed for other values of J.

Important: Understand physics at "high B - low T" limit and "weak B - high T" limit.

What about Curie's law?



$$\frac{\mu_B B}{kT} \sim \frac{10^{-4}\,\text{eV}}{\frac{1}{40}\,\text{eV}} \ll 1$$ room temp

focus on here!

Weak-field and/or high T
room temp.

$$\tanh\left(\frac{\mu_B B}{kT}\right) \approx \frac{\mu_B B}{kT}$$

($\tanh x \approx x$ for $x \ll 1$)

$$M = \mathcal{N}\mu_B \cdot \frac{\mu_B B}{kT} = \frac{\mathcal{N}\mu_B^2}{kT} B$$

($\sim \frac{1}{T}$ behavior shows up!)

$$\approx \underbrace{\frac{\mathcal{N}\mu_B^2 \mu_0}{kT}}_{} \cdot H \quad (\because B = \mu_0 \mu_r H \approx \mu_0 H)$$

$$= \chi H \quad \text{with } \chi = \frac{\mathcal{N}\mu_B^2 \mu_0}{kT} \quad (\text{for } J=\tfrac{1}{2})$$

and Curie's law follows!

Remark: Rewrite in more general form

$$\chi = \frac{\mathcal{N}\mu_B^2 \mu_0}{kT} \quad (J = \tfrac{1}{2})$$

$$= \frac{\mathcal{N}(g\mu_B)^2 \mu_0}{4kT} \quad (\because g = 2 \text{ for } J = \tfrac{1}{2})$$

$$= \frac{\mathcal{N}(g\mu_B)^2 \mu_0}{3kT} \cdot \frac{1}{2}\left(\frac{1}{2}+1\right)$$

$$= \frac{\mathcal{N}(g\mu_B)^2 \mu_0\, J(J+1)}{3kT}$$

[a form of χ good for other values of J]

$\sim \frac{1}{T}$ behavior persists

$\langle E \rangle$ and average energy per ion/atom

Physical reasoning

$$\langle E_{\text{per ion}} \rangle = \underbrace{(-\mu_B B)}_{\text{lower energy}} \cdot \underbrace{\frac{1}{Z} e^{\beta\mu_B B}}_{\substack{\text{prob. of alignment} \\ \text{(bigger)}}} + \underbrace{(+\mu_B B)}_{\text{higher energy}} \underbrace{\frac{1}{Z} e^{-\beta\mu_B B}}_{\substack{\text{prob. of anti-alignment} \\ \text{(smaller)}}}$$

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

make sense!

Same as plugging formula

$$\langle E_{\text{per ion}} \rangle = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_B = \left(-\frac{\partial}{\partial \beta} \ln Z\right)_B$$

or

$$\langle E \rangle_{\text{whole system}} = \left(-\frac{\partial}{\partial \beta} \ln Z\right)_B = N \langle E_{\text{per ion}} \rangle$$

Refs: The coverage here is more than that in Simon's "The Oxford Solid State Basics" (Ch. 19) on paramagnetism. See also the Solid State physics textbooks by Kittel and by Christman.

Summary: $\vec{\mu}_J = -g\frac{\mu_B}{\hbar}\vec{J}$, $\mu_z = -g\mu_B m_J$, $\vec{B} = B\hat{z}$, $\mathcal{H} = -\vec{\mu}_J\cdot\vec{B} = g\mu_B m_J B$

$J = 1/2$ case ($g=2$, ∵ spin contribution only)

- Form a table:

m_J	μ_z	$\mathcal{H} = -\mu_z B$		Prob. of finding atom
$+1/2$	$-\mu_B$	$\mu_B B$	"anti-aligned"	$\frac{1}{z}e^{-\beta\mu_B B}$
$-1/2$	$+\mu_B$	$-\mu_B B$	"aligned"	$\frac{1}{z}e^{\beta\mu_B B}$

$$z = e^{\beta\mu_B B} + e^{-\beta\mu_B B} = 2\cosh(\beta\mu_B B) \;;\quad Z = z^N$$

$$\langle\mu_z\rangle = -\mu_B\frac{e^{-\beta\mu_B B}}{z} + \mu_B\frac{e^{\beta\mu_B B}}{z} = \mu_B\tanh(\beta\mu_B B)$$

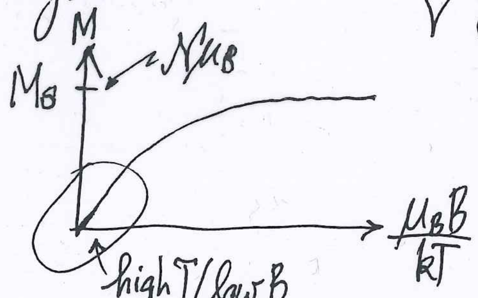
magnetisation

Note: $\langle\mu_z\rangle = \frac{1}{\beta}\frac{\partial\ln z}{\partial B}$, $\mathcal{M} = N\langle\mu_z\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial B}$, $M = \frac{1}{V}\frac{1}{\beta}\frac{\partial\ln Z}{\partial B} = -\frac{1}{V}\frac{\partial F}{\partial B}$

magnetic moment in whole system

N/V

$$M = \mathcal{N}\mu_B\tanh(\beta\mu_B B)$$



But $\mu_B \sim 10^{-5}$ eV/Telsa

$B \sim$ a few Telsa or less

$\mu_B B \ll kT$ (room temp.)

$$M \approx \mathcal{N}\mu_B\frac{\mu_B B}{kT} = \underbrace{\mathcal{N}\frac{\mu_B^2\mu_0}{kT}}_{\chi\,\sim\,\frac{1}{T}\text{ (Curie's law)}} H$$

$$\langle E\rangle_{\text{one atom}} = \mu_B B\frac{e^{-\beta\mu_B B}}{z} + (-\mu_B B)\frac{e^{\beta\mu_B B}}{z} = -\mu_B B\tanh(\beta\mu_B B) = -\frac{\partial\ln z}{\partial\beta}$$

$$\langle E\rangle_{\text{whole system}} = \underbrace{-N\mu_B B\tanh(\beta\mu_B B)}_{-\mathcal{M}\cdot B} = -N\frac{\partial\ln z}{\partial\beta} = -\frac{\partial\ln Z}{\partial\beta}$$

General J

$\vec{B} = B\hat{z}$

Form a table: $\vec{\mu}_J = -g\mu_B\frac{\vec{J}}{\hbar}$, $\mu_z = -g\mu_B m_J$, $\varepsilon = -\mu_z B = g\mu_B m_J B$

	m_J	μ_z	energy	Prob. of finding moment
	$+J$	$-g\mu_B J$ (least aligned) "anti-aligned"	$g\mu_B BJ$	$\frac{1}{z}e^{-\beta g\mu_B BJ}$ (smallest)
	⋮		⋮	⋮
"general"	m_J	$-g\mu_B m_J$	$g\mu_B B m_J$	$\frac{1}{z}e^{-\beta g\mu_B B m_J}$
	⋮		⋮	⋮
	$-J$	$+g\mu_B J$ (best aligned)	$-g\mu_B BJ$	$\frac{1}{z}e^{\beta g\mu_B BJ}$ (biggest)

$2J+1$ values of m_J

$2J+1$ states as $2J+1$ degeneracy removed by B-field

$$z = \sum_{m_J=-J}^{+J} e^{-\beta g\mu_B B m_J}$$

can be summed up exactly $\sum_{n=0}^{N} x^n = \frac{1-x^{N+1}}{1-x}$

and

$$M = -\frac{1}{V}\frac{\partial F}{\partial B}$$

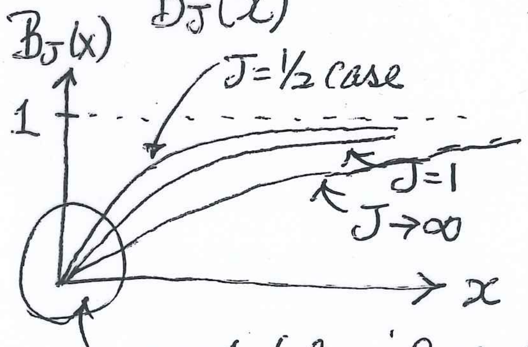
OR $\langle\mu_z\rangle = \sum_{m_J=-J}^{J}(-g\mu_B m_J)\frac{1}{z}e^{-\beta g\mu_B B m_J}$

and $M = \frac{N}{V}\langle\mu_z\rangle$

General value of J

- The following pages for any value of J ($J = 1/2, 1, 3/2, 2, 5/2, \ldots$) are an extension of the $J = 1/2$ discussion. This part is optional.
- The method is the same as the $J = 1/2$ case.
- The result is:

$$M = \underbrace{M_S}_{\substack{\text{saturation magnetisation} \\ (\mathcal{N} g \mu_B J)}} \cdot \underbrace{B_J\left(\frac{g\mu_B B J}{kT}\right)}_{\substack{\text{Brillouin function of order } J \\ B_J(x)}}$$



$x \ll 1$ (low field, high T)

$$\underbrace{B_J(x) \sim x}_{\text{Gives } M = \chi H}$$

with $\chi \sim \frac{1}{T}$ Curie's law

(b) General value of J

Physical argument:

- prob. for occupying an energy level $(\underbrace{g\mu_B B m_J}_{(\text{thus } \mu_z = -g\mu_B m_J)})$ is given by

$$\frac{e^{-\frac{g\mu_B m_J B}{kT}}}{\sum_{m_J=-J}^{J} e^{-g\mu_B m_J B/kT}}$$

← one-particle partition fn z

$$\therefore M = \frac{\mathcal{N} \sum_{m_J=-J}^{J} \mu_{z,m_J} e^{-g\mu_B m_J B/kT}}{\sum_{m_J=-J}^{J} e^{-g\mu_B m_J B/kT}} = \frac{\mathcal{N} \sum_{m_J=-J}^{J} (-\mu_B g m_J) e^{-g\mu_B m_J B/kT}}{\sum_{m_J=-J}^{J} e^{-g\mu_B m_J B/kT}}$$

$$\mathcal{N} = \frac{\#\text{ atoms}}{\text{Volume}} = \frac{N}{V}$$

- Check result against $J = 1/2$ case

More systematically:

- N independent, distinguishable particles in volume V

$$Z = (z)^N$$

$$z = \sum_{m_J=-J}^{J} e^{-\beta g \mu_B m_J B}$$

⌜ $\underline{\text{Recall}}$ (Geometric series)

$$\sum_{n=0}^{N} x^n = 1 + x + x^2 + \cdots + x^N$$

$$= 1 + x + x^2 + \cdots \overset{\swarrow \text{ to } \infty}{} - x^{N+1} - x^{N+2} - \cdots$$

$$= (1 + x + x^2 + \cdots)(1 - x^{N+1})$$

$$= \frac{1 - x^{N+1}}{1 - x}$$ ⌟

Writing $x \equiv \beta g \mu_B J B$, we have $z = e^{x} \sum_{n=0}^{2J} e^{-\frac{x}{J} n}$

$$z = e^{x} \frac{\left(1 - e^{-(2J+1)\frac{x}{J}}\right)}{1 - e^{-\frac{x}{J}}}$$ (Ex.) [must try this!]

$$= \frac{\sinh\left[\left(\frac{2J+1}{2J}\right) \cdot x\right]}{\sinh\left(\frac{x}{2J}\right)}$$ (Ex.)

Recall, $\langle \mu_z \rangle = \frac{1}{\beta}\left(\frac{\partial \ln z}{\partial B}\right)_\beta$ for one ion (see p. VI-23)

$$\therefore M = \frac{N}{V} \frac{1}{\beta}\left(\frac{\partial \ln z}{\partial B}\right)_\beta = \frac{1}{V}\frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial B}\right)_\beta$$

magnetic moment in z-direction per volume

$$= \mathcal{N} \frac{1}{\beta}\left[\frac{\partial}{\partial B} \ln\left(\frac{\sinh\left[\frac{2J+1}{2J} \cdot x\right]}{\sinh \frac{x}{2J}}\right)\right]$$

Note: $x = \beta g \mu_B J B$

$$= \mathcal{N} g \mu_B J \underbrace{\left(\frac{2J+1}{2J} \coth\left[\frac{2J+1}{2J} x\right] - \frac{1}{2J} \coth \frac{x}{2J}\right)}$$ (Ex.)

$$\Rightarrow \underset{M(B,T)}{M} = \underbrace{\mathcal{N} g \mu_B J}_{M_s} \; \underbrace{B_J(x)}$$ (General value of J)

$B_J(x)$: Brillouin function of order J

M_s = saturation magnetization (as $B_J(x) \to 1$ as $x \gg 1$)

- In terms of $F = -kT \ln Z = -NkT \ln z = -\frac{N}{\beta} \ln z$,

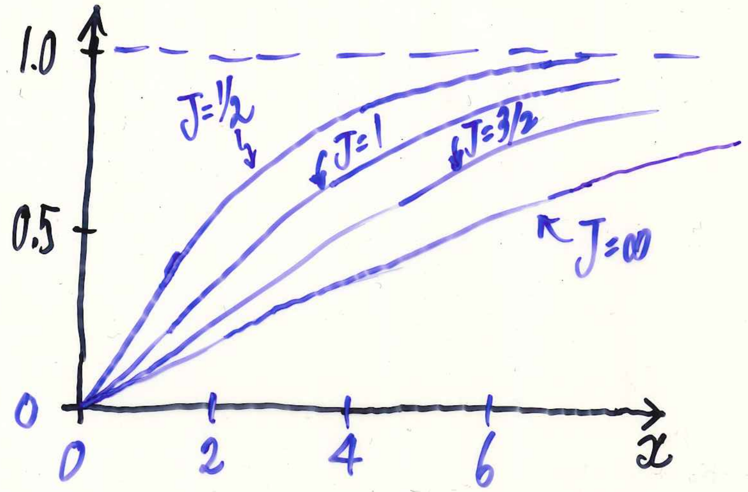
$$M = -\frac{1}{V}\left(\frac{\partial F}{\partial B}\right)_T$$

In dealing with magnetic systems in statistical mechanics, the free energy is taken to be $dF = -S\,dT - \vec{\mathcal{M}} \cdot d\vec{B}$.

$\vec{\mathcal{M}}$: total magnetic moment in system.

See Adkins, "Equilibrium Thermodynamics" and Mandl, "Statistical Physics" for discussions on magnetic systems.

Brillouin function $B_J(x)$:



$J=\frac{1}{2}$ case: $B_J(x) = \tanh x$

$B_J(x) \to 1$ for large x

(i) When $x = \frac{g\mu_B J B}{kT} \gg 1$ (high field, low T)

$\coth x \to 1, \quad x \to \infty$

$$B_J(x) \approx \left(1+\frac{1}{2J}\right) - \frac{1}{2J} = 1$$

$$M \approx \mathcal{N} g \mu_B J = M_s$$

$\Rightarrow$ Each atom takes on the maximum z-component of $\vec{\mu}$

(ii) When $x = \frac{g\mu_B J B}{kT} \ll 1$ (low field, high T)

$$\left(\coth x \approx \frac{1}{x} - \frac{1}{3}x + O(x^3) \; ; \; x \ll 1\right)$$

$$B_J(x) \approx \frac{J+1}{3J}\, x \propto x \propto B \quad \text{(Ex.)}$$

$$M \cong \frac{\mathcal{N}(g\mu_B)^2 J(J+1)}{3kT} B$$

$$= \underbrace{\frac{\mathcal{N}(g\mu_B)^2 \mu_0 J(J+1)}{3kT}} H$$

$$= \chi \; H$$

$$\chi = \underbrace{\frac{\mathcal{N}(g\mu_B)^2 \mu_0 J(J+1)}{3k}}_{\text{Curie's constant}} \cdot \frac{1}{T} \qquad \text{Curie's law}$$

(can be extracted exp'tally and calculated theoretically)

$\therefore$ stat. mech. (plus QM) gives a microscopic theory of paramagnetism.

(c) <u>How about $J \to \infty$?</u>

m_J: infinitely many possible values

$\Rightarrow$ quantization of μ_z becomes unimportant

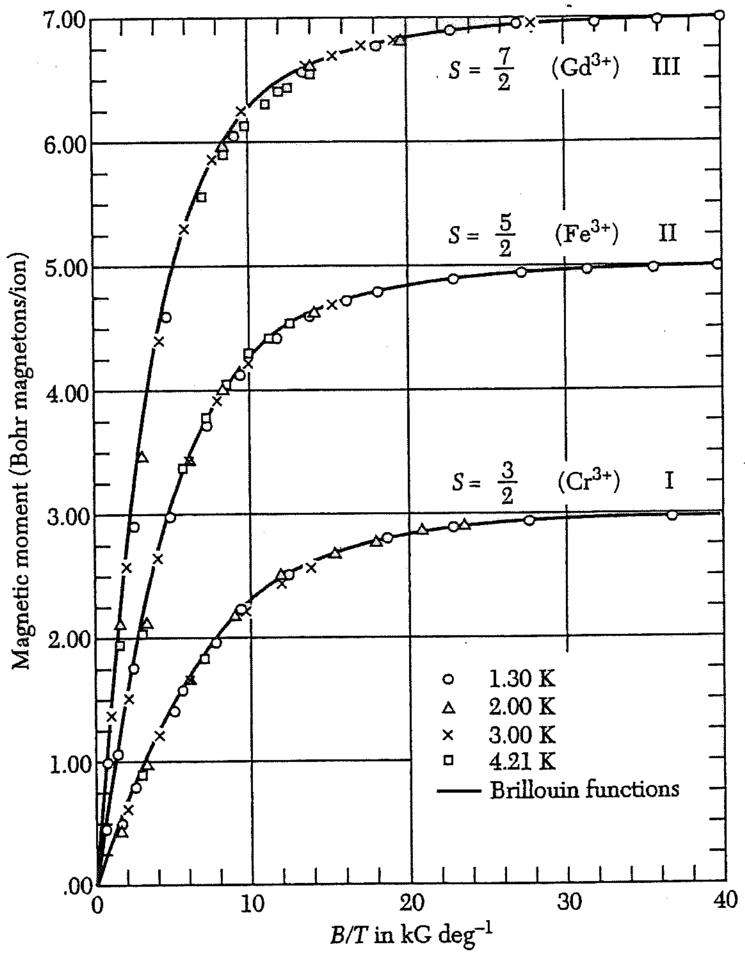
- In the limit $J \to \infty$ in such a way that $Jg\mu_B \to$ finite, we have the <u>classical limit</u>

$$B_J(x) \approx \coth x - \frac{1}{x} \equiv \underbrace{L(x)}_{\text{Langevin function}}$$

At high T, we can still obtain

$$M = \frac{C}{T} H \qquad \text{Curie's law}$$

And the theory works!



Plot of magnetic moment versus B/T for spherical samples of (I) potassium chromium alum, (II) ferric ammonium alum, and (III) gadolinium sulfate octahydrate. Over 99.5% magnetic saturation is achieved at 1.3 K and about 50,000 gauss (5T).

(From Kittel's "Introduction to Solid State Physics")