Simple Quantum Paramagnet, Canonical Ensemble

Origin of magnetic moments:

Electron spin and orbital angular momentum

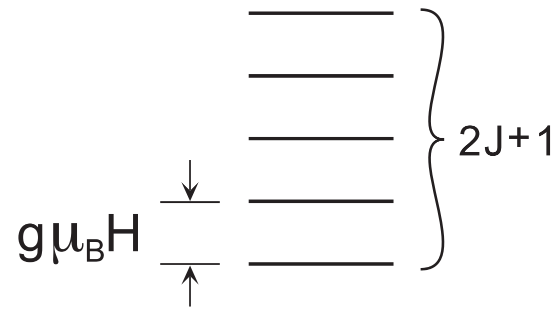
$$\vec{S} + \vec{L} \equiv \vec{J} \qquad \vec{\mu} = g_J \mu_B \vec{J} \qquad \mu_B \equiv e\hbar/2m_e c$$

Nuclear angular momentum

$$\vec{I} \qquad \vec{\mu} = g_I \mu_N \vec{I} \qquad \mu_N \equiv e\hbar/2m_p c$$

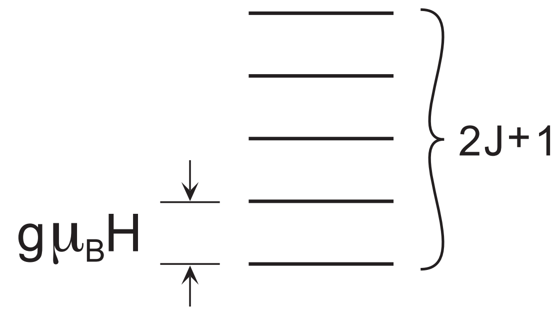
$$\epsilon_m = -g\mu_B H\, m$$

$$m = J, J-1, \cdots -J$$



$$\epsilon_m = -g\mu_B H\, m$$

$$m = J, J-1, \cdots - J$$



$$Z_1(T,H) = \sum_{m=-J}^{J} e^{-\epsilon_m/kT} = \sum_{m=-J}^{J} (e^{\eta})^m = \frac{\sinh[(J+\frac{1}{2})\eta]}{\sinh[\frac{1}{2}\eta]}$$

$$\eta \equiv \frac{g\mu_B H}{kT} = \frac{\text{level spacing}}{kT}$$

Note $Z_1 = Z_1(\eta)$ $\quad Z = Z_1(\eta)^N = Z(\eta)$ at fixed N

$$p(m) = e^{-\epsilon_m/kT}/Z_1 = e^{\eta\, m}/Z_1$$

$$< \mu > = \sum_m \frac{(g\mu_B m)e^{\eta\, m}}{Z_1} = g\mu_B \left(\frac{1}{Z_1}\frac{\partial Z_1}{\partial \eta} \right)$$

$$\equiv g\mu_B J B_J(\eta) \qquad M = N < \mu >= g\mu_B N J B_J(\eta)$$

$$B_J(\eta) = \frac{1}{J}\left(\frac{1}{Z_1}\frac{\partial Z_1}{\partial \eta} \right)$$

$$= \underline{\frac{1}{J}\left\{ (J+\frac{1}{2}) \coth[(J+\frac{1}{2})\,\eta] - \frac{1}{2}\coth[\frac{1}{2}\,\eta] \right\}}$$

This is called the "Brillouin Function".

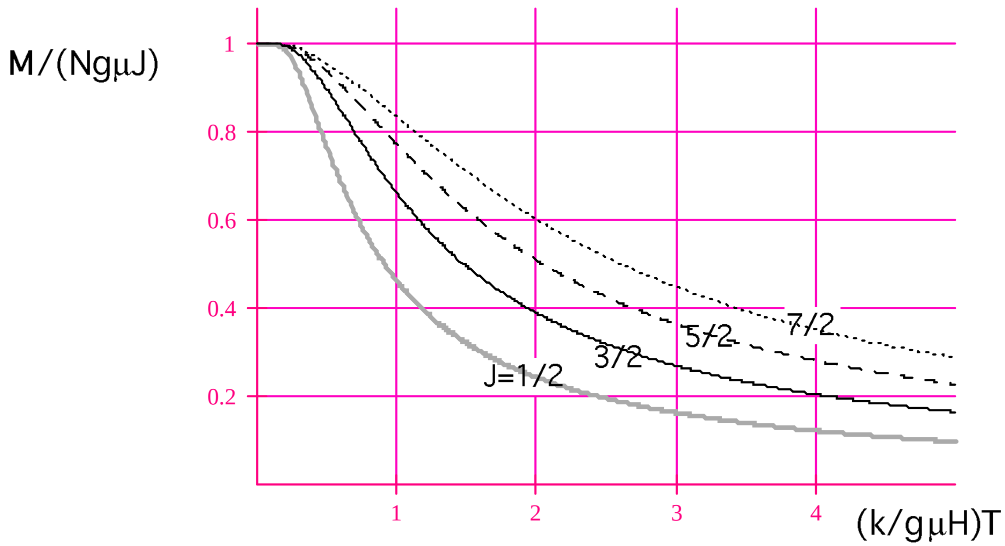
$$\coth x \to \frac{1}{x} + \frac{x}{3} \qquad x \ll 1 \qquad \lim_{\eta \to 0} B_J(\eta) = \frac{J+1}{3}\eta$$

$$\coth x \to 1 + 2e^{-2x} \quad x \gg 1 \qquad \lim_{\eta \to \infty} B_J(\eta) = 1 - \frac{e^{-\eta}}{J}$$

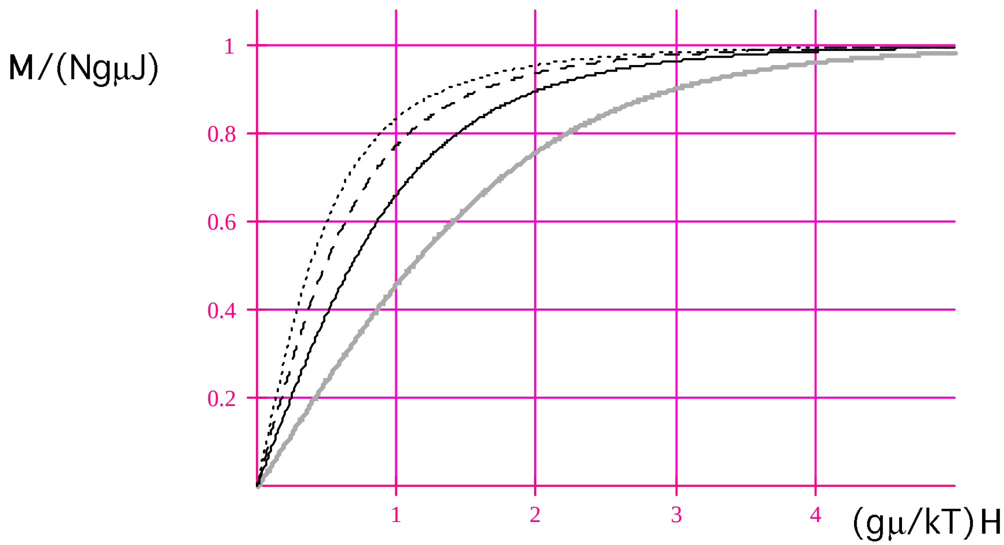
$$M \;\to\; N\,\frac{(g\mu_B)^2 J(J+1)}{3}\,\frac{H}{kT} \qquad \text{High T (Curie Law)}$$

$$\;\to\; N\,g\mu_B J\left(1 - \frac{1}{J}\,e^{-\eta}\right) \qquad \text{Low T (Energy Gap)}$$

MAGNETIZATION OF A QUANTUM PARAMAGNET



Field Held Constant



Temperature Held Constant

Note: T and H enter only through $\eta \equiv \dfrac{g\mu_B H}{kT}$

$$\left(\frac{\partial \eta}{\partial H}\right)_T = \frac{\eta}{H} \qquad \left(\frac{\partial \eta}{\partial T}\right)_H = -\frac{\eta}{T}$$

We now show that this $\Rightarrow U = 0$.

$$
\begin{aligned}
dU &= TdS + HdM \\
&= T\left(\left(\frac{\partial S}{\partial T}\right)_H dT + \left(\frac{\partial S}{\partial H}\right)_T dH\right) + H\left(\left(\frac{\partial M}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial H}\right)_T dH\right) \\
&= \underbrace{\left(T\left(\frac{\partial S}{\partial T}\right)_H + H\left(\frac{\partial M}{\partial T}\right)_H\right)}_{0} dT + \underbrace{\left(T\left(\frac{\partial S}{\partial H}\right)_T + H\left(\frac{\partial M}{\partial H}\right)_T\right)}_{0} dH \\
&= 0 \quad \text{for all paths} \Rightarrow U = 0
\end{aligned}
$$

$$
\begin{aligned}
T\left(\frac{\partial S}{\partial T}\right)_H + H\left(\frac{\partial M}{\partial T}\right)_H &= T \underbrace{\left(\frac{\partial S}{\partial T}\right)_H}_{S'(\eta)(-\eta/T)} + H \underbrace{\left(\frac{\partial S}{\partial H}\right)_T}_{S'(\eta)(\eta/H)} \\
&= -\eta S'(\eta) + \eta S'(\eta) \\
&= 0
\end{aligned}
$$

A similar expansion shows that the other term is also zero.

Internal Energy

$$dU = đQ + đW = TdS + HdM$$

$dU \equiv$ adiabatic ($đQ = 0$) work

$$đQ = TdS, \quad đQ = 0 \Rightarrow dS = 0 \Rightarrow dM = 0 \Rightarrow dU = 0$$

$dU = 0$ for any change: $U = 0$ for this model

But $E \equiv N < \epsilon >= -HM \neq 0$!!

Energy = energy to create H field ①

+ energy to assemble M ②

+ energy to move M into H ③

(1) does not appear when using $\not{d}W = HdM$.

(2) We did not create the $\vec{\mu}$. They do not interact.
$\Rightarrow U = 0$ in the current example.

(3) $-\vec{H} \cdot \vec{M}$, energy of macroscopic moment in $\vec{H}$ equals $N < \epsilon >$ in the current example.

So what's the result?

$$< \mathcal{H} >^{\text{S. M.}} \neq U^{\text{Thermo}}$$

$$= U^{\text{assembly}} + (-\vec{H} \cdot \vec{M})^{\text{position}} \quad (\text{for } đW = HdM)$$

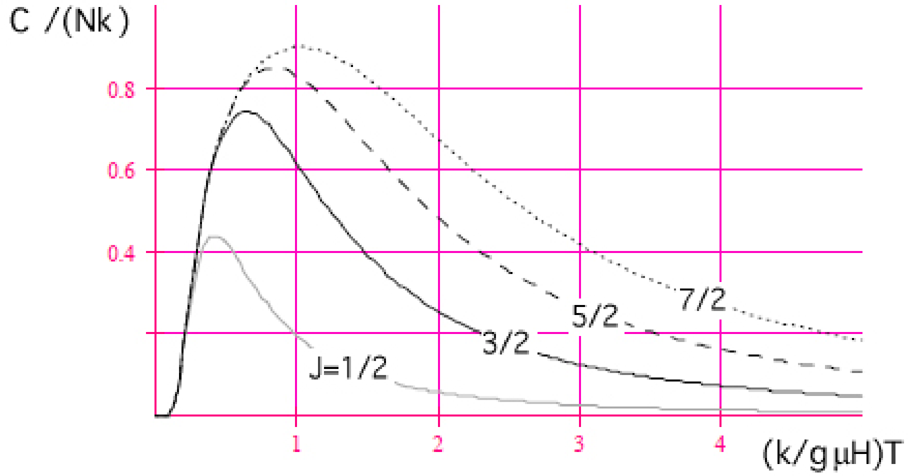
$$< \mathcal{H} > = -\frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)_H = -\underbrace{\frac{1}{Z}\frac{dZ}{d\eta}}_{M/g\mu_B} \underbrace{\left(\frac{\partial \eta}{\partial \beta}\right)_H}_{g\mu_B H} = -HM \quad \surd$$

$$C_M \equiv \left(\frac{đQ}{dT}\right)_M = T\left(\frac{\partial S}{\partial T}\right)_M = 0 \text{ since } S = S(M)$$

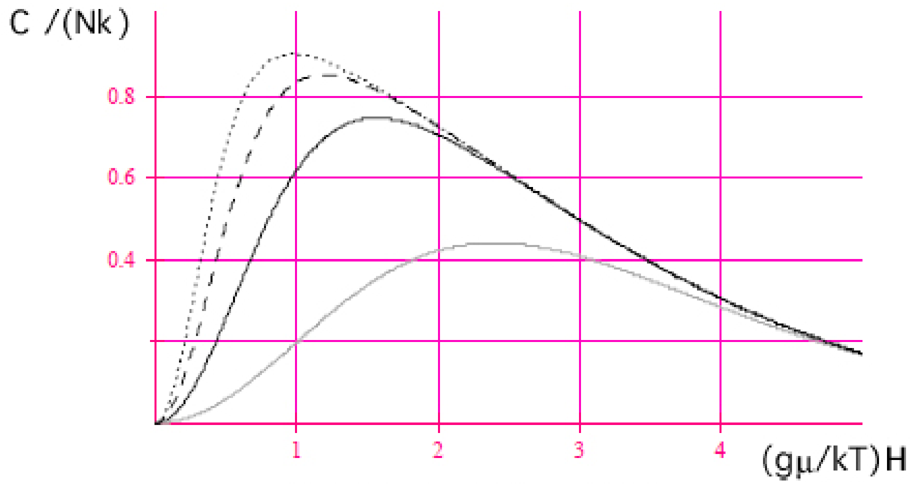
$$C_H \equiv \left(\frac{đQ}{dT}\right)_H = \frac{1}{T}\left(\underbrace{dU}_{0} - H\,dM\right)_H = -H\left(\frac{\partial M}{\partial T}\right)_H$$

$$= \underline{NkJ\eta^2 B'_J(\eta)}$$

HEAT CAPACITY OF A QUANTUM PARAMAGNET



Field Held Constant



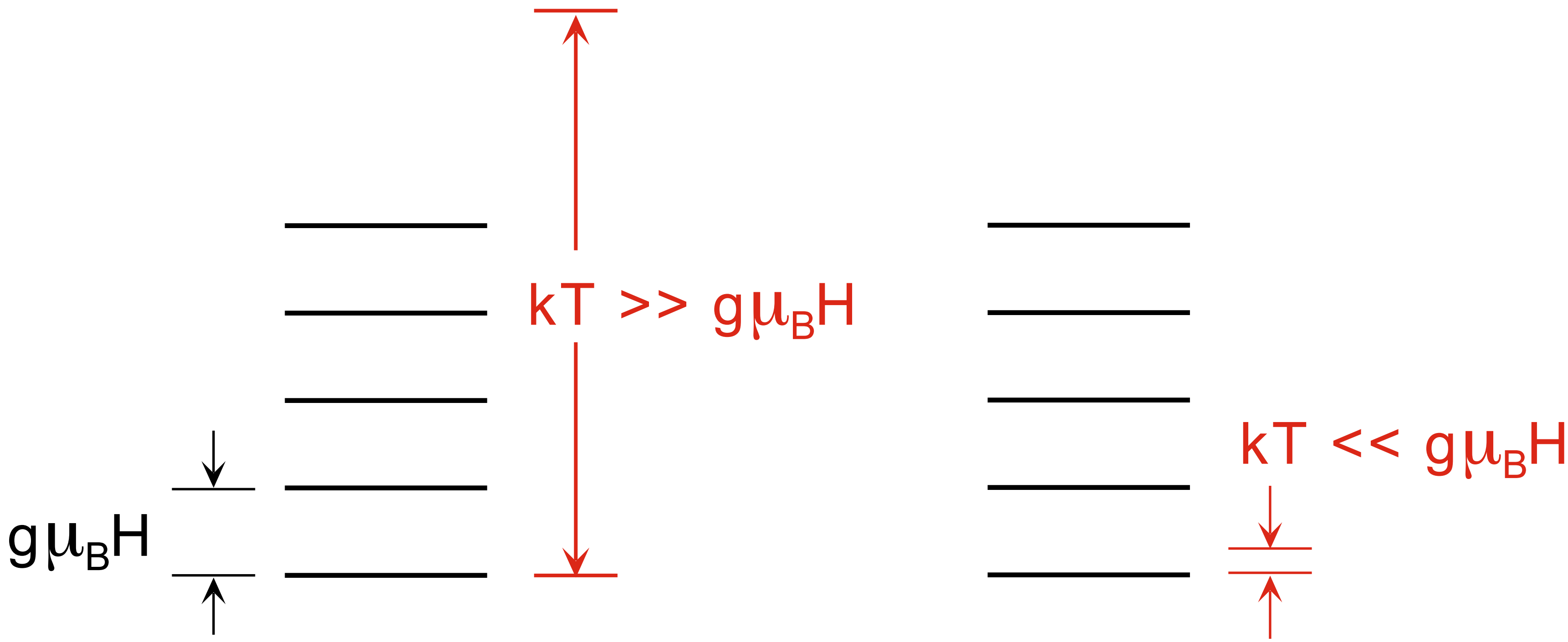
Temperature Held Constant

Entropy of a Quantum Paramagnet

- When is $-kT \ln Z \neq F$?

- How is a paramagnet like a sponge?

HIGH AND LOW TEMPERATURE BEHAVIOR OF A QUANTUM PARAMAGNET



ENERGY LEVELS ALMOST EQUALLY POPULATED, CURIE LAW BEHAVIOR

MOMENT ALMOST MAXIMUM, ENERGY GAP BEHAVIOR

$$S(kT \ll g\mu_B H) \rightarrow Nk\,\mathrm{ln}(1) = 0$$

$$S(kT \gg g\mu_B H) \rightarrow Nk\,\mathrm{ln}(2J+1)$$

$$Z_1 = \sum_{m=-J}^{J} (e^{\eta})^m \qquad \eta \equiv g\mu_B H/kT$$

Try

$$-kT\,\mathrm{ln}\,Z \;=\; F = \underbrace{U}_{0} - TS \Rightarrow S = k\,\mathrm{ln}\,Z = Nk\,\mathrm{ln}\,Z_1$$

$$S(kT \ll g\mu_B H) \rightarrow Nk \ln(1) = 0$$

$$S(kT \gg g\mu_B H) \rightarrow Nk \ln(2J+1) \quad \underline{Nk \ln(2J+1) \;\; \text{O.K.}}$$

$$Z_1 = \sum_{m=-J}^{J} (e^{\eta})^m \qquad \eta \equiv g\mu_B H/kT$$

Try

$$-kT \ln Z = F = \underbrace{U}_{0} - TS \Rightarrow S = k \ln Z = Nk \ln Z_1$$

$$S(kT \ll g\mu_B H) \rightarrow Nk\ln(1) = 0 \quad \underline{NkJ(g\mu_B H/kT) \;\; \text{wrong!}}$$

$$S(kT \gg g\mu_B H) \rightarrow Nk\ln(2J+1) \quad \underline{Nk\ln(2J+1) \;\; \text{O.K.}}$$

$$Z_1 = \sum_{m=-J}^{J} (e^{\eta})^m \qquad \eta \equiv g\mu_B H/kT$$

Try

$$-kT\ln Z \underbrace{=}_{} F = \underbrace{U}_{0} - TS \Rightarrow S = k\ln Z = \underbrace{Nk\ln Z_1}_{}$$

wrong ______________ $\Leftarrow$ ______________ wrong

In the derivation of the canonical ensemble we found

$$-kT \ln Z =< E_1 > -TS_1 \text{ where } < E_1 >=< \mathcal{H}(\{p,q\}) >$$

Then we set $< E_1 >= U$. But in the paramagnet $< E_1 >= U - HM$, thus

$$-kT \ln Z = U - HM - TS = G(T,H) \text{ for our model.}$$

$$\Rightarrow S = k \ln Z - HM/T \underbrace{\rightarrow}_{T\rightarrow 0} \underline{Nk \ln Z_1 - H(Ng\mu_B J)/T}$$

In general for magnetic systems, even when $U \neq 0$,

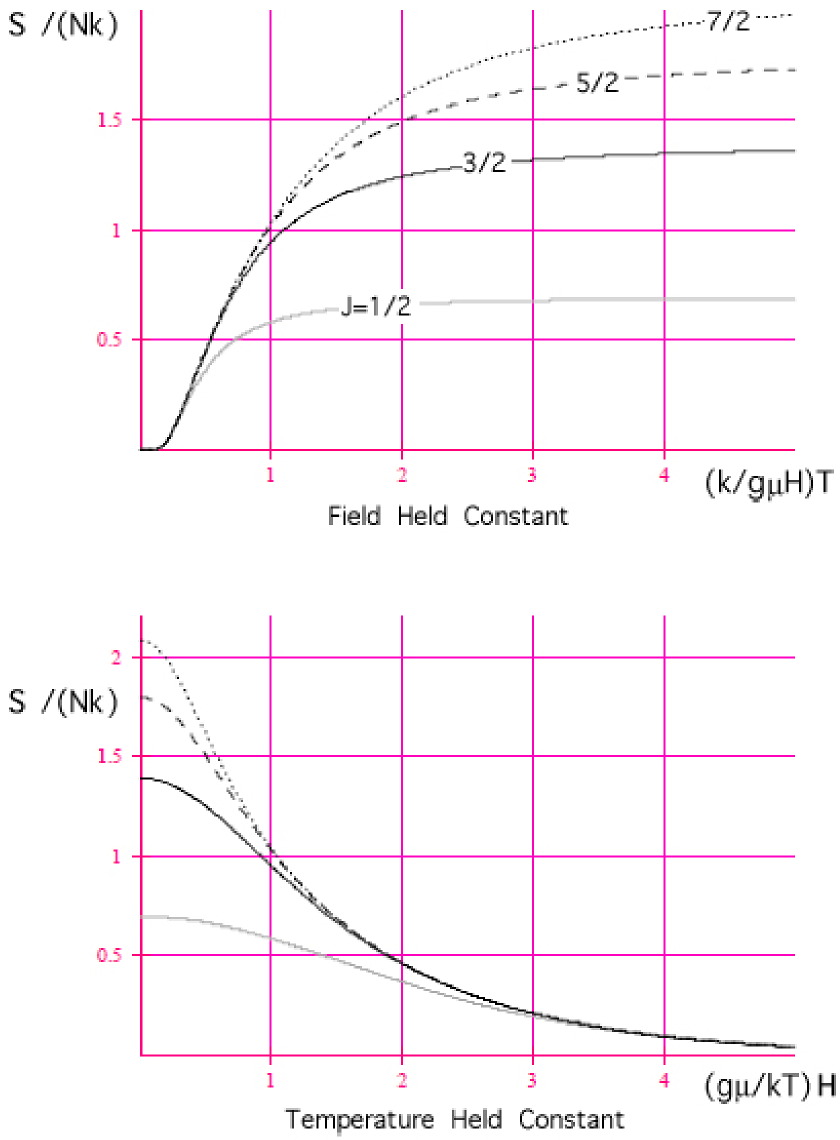
$$dG = -SdT - MdH$$

$$G(T,H) = -k_B T \ln Z$$

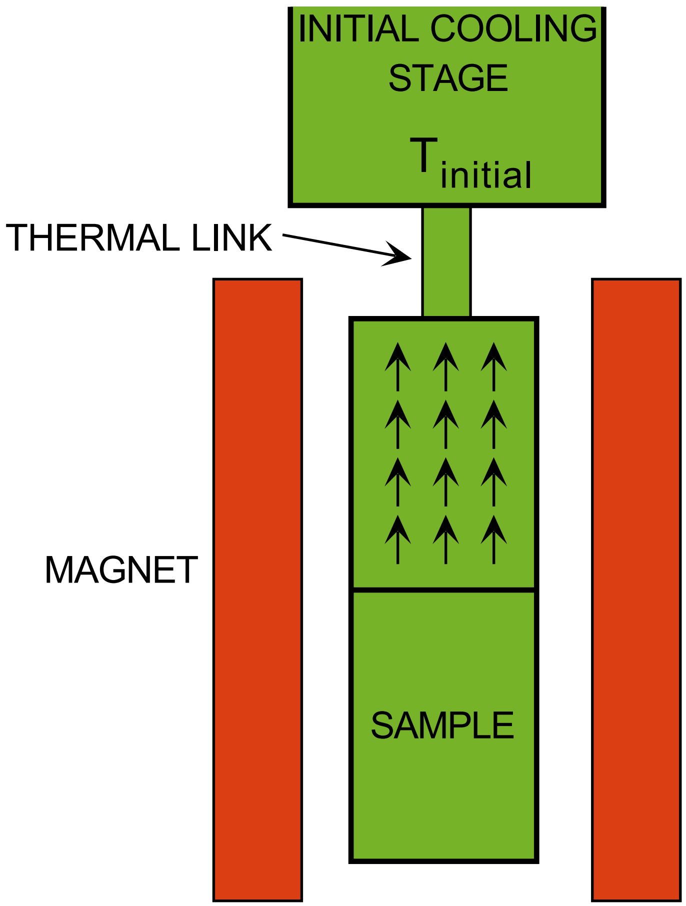
$$M(T,H) \;=\; -\left(\frac{\partial G}{\partial H}\right)_T$$

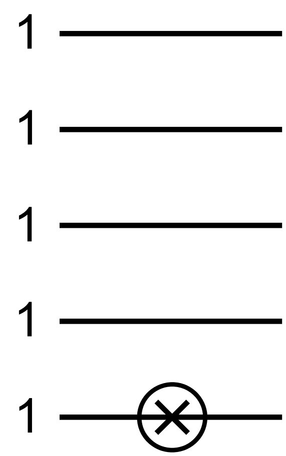
$$S(T,H) \;=\; -\left(\frac{\partial G}{\partial T}\right)_H$$

ENTROPY OF A QUANTUM PARAMAGNET



ADIABATIC DEMAGNETIZATION (MAGNETIC COOLING)





$$kT \ll g\mu_B H$$

$H = H_{initial}$

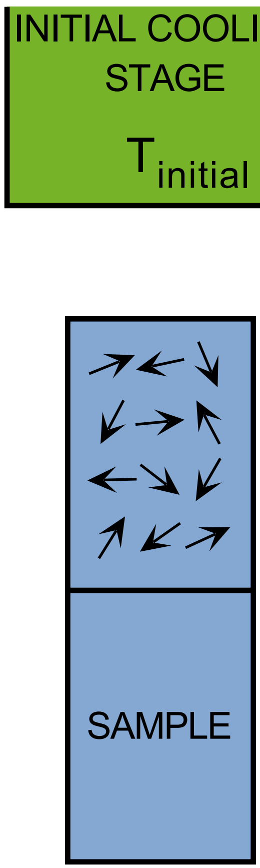
$S_M \sim 0$

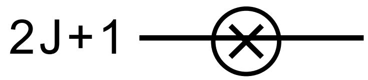
S_S high

$\}$ S_{total}

$T_S = T_{initial}$

ADIABATIC DEMAGNETIZATION
(MAGNETIC COOLING)





$kT >> g\mu_B H$

$H \sim 0$

$S_M \sim Nk\ln(2J+1)$ } S_{total}

S_S low

$T_S << T_{initial}$

Electronic Example, CMN

Cerium Mangesium Nitrate

$$2Ce(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$$

Ce^{+++} $J=5/2$ $T_{\text{ordering}} \sim 1.9$ mK

Cools ^{3}He and samples therein to ~ 2 mK.

Nuclear Example, Cu

Metallic Copper

Cu I=3/2 $T_{\text{ordering}} \sim 1\ \mu$K

Cools Cu electrons and lattice to $\sim 10\ \mu$K.

8.044 Statistical Physics I
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