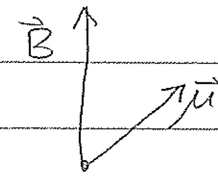
Paramagnet



magnetic dipole moment $\vec{\mu}$
in magnetic field $\vec{B} = B\hat{z}$

energy: $\varepsilon = -\vec{\mu}\cdot\vec{B}$

classical magnetic dipole

configuration space: (θ, ϕ) $\quad \vec{\mu} = \mu \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$

energy: $\varepsilon = -\mu B \cos\theta$

quantum magnetic dipole

dipole moment operator: $\vec{\mu} = g \frac{e}{2m_e c} \vec{J}$

angular momentum operator: $\vec{J}$

eigenvalues: $\vec{J}^2 = j(j+1)\hbar^2 \quad j = 0$ or $\frac{1}{2}$ or 1 or ...
$J_z = m\hbar \quad m = -j, -j+1, \ldots, +j$

energies: $\varepsilon = -m\, g \frac{e\hbar}{2m_e c}$

Classical paramagnet with N spins

Hamiltonian: $H = \sum_{n=1}^{N} (-\mu B \cos\theta_n)$

partition function: $Z_N = Z_1^N$

$$Z_1 = \int d\Omega \, e^{-\beta(-\mu B \cos\theta)}$$

$$= \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi \, e^{\beta\mu B \cos\theta}$$

$$= 2\pi \int_{-1}^{+1} d\cos\theta \, e^{\beta\mu B \cos\theta}$$

$$= 2\pi \frac{1}{\beta\mu B} \left(e^{+\beta\mu B} - e^{-\beta\mu B} \right)$$

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

Helmholtz free energy: $F = -\frac{1}{\beta} \log Z_N$

$$= -NT \left[\log(\sinh(\beta\mu B)) - \log(\beta\mu B) + \log(4\pi) \right]$$

thermodynamic relation: $dF = -S\,dT - M\,dB$

magnetization: $M = -\frac{\partial F}{\partial B} = +\frac{\partial}{\partial B}(T \log Z_N)$

$$= N\mu \left[\frac{1}{\tanh(\beta\mu B)} - \frac{1}{\beta\mu B} \right]$$

average energy: $U = -\frac{\partial}{\partial\beta} \log Z_N = -MB$

Spin-$\frac{1}{2}$ Quantum Paramagnet with N spins

magnetic moment operator: $\vec{\mu} = g \frac{e}{2m_e c} \vec{S}$

spin operator: $\vec{S}$ $\quad \vec{S}^2 = \frac{3}{4}\hbar^2$

$$S_z = +\tfrac{1}{2}\hbar \text{ or } -\tfrac{1}{2}\hbar$$

$$\mu_z = \pm\mu, \quad \mu = \frac{g}{2}\frac{e\hbar}{2m_e c}$$

partition function: $Z_N = Z_1^N$

$$Z_1 = \sum_{\pm} e^{-\beta(\mp\mu)B}$$

$$= e^{+\beta\mu B} + e^{-\beta\mu B} = 2\cosh(\beta\mu B)$$

Helmholtz free energy: $F = -\frac{1}{\beta}\log Z_N$

$$= -NT\log\big(2\cosh(\beta\mu B)\big)$$

$$dF = -S\,dT - M\,dB$$

magnetization: $M = -\frac{\partial F}{\partial B} = +\frac{\partial}{\partial B}\left(T\log Z_N\right)$

$$= N\mu\tanh(\beta\mu B)$$

average energy: $U = -\frac{\partial}{\partial\beta}\log Z = -MB$

entropy: $S = -\frac{\partial F}{\partial T} = +\frac{\partial}{\partial T}\left[NT \log(2\cosh(\beta\mu B))\right]$

$= N\left[\log(2\cosh(\beta\mu B)) - \beta\mu B \tanh(\beta\mu B)\right]$

<u>macrostates</u> characterized by M

minimum energy: $M = +N\mu$ all dipoles aligned with $\vec{B}$

one microstate: $m_1 = m_2 = \cdots = m_N = +\frac{1}{2} \implies S = 0$

zero energy: $M = 0$ half dipole aligned, half antialigned

microstates: $m_n = +\frac{1}{2}$ for half of dipole, $-\frac{1}{2}$ for other half

number of microstate: $\binom{N}{N/2} = \frac{N!}{\left[\left(\frac{N}{2}\right)!\right]^2}$

entropy: $S = \log(N!) - 2\log\left(\frac{N}{2}!\right)$

$\simeq (N\log N - N) - 2\left(\frac{N}{2}\log\frac{N}{2} - \frac{N}{2}\right)$

$= N\log 2$

maximum energy: $M = -N\mu$ all dipoles anti-aligned

one microstate: $m_1 = m_2 = \cdots = m_N = -\frac{1}{2} \implies S = 0$

express S as function of M

eliminate β using $M = N\mu \tanh(\beta\mu B)$

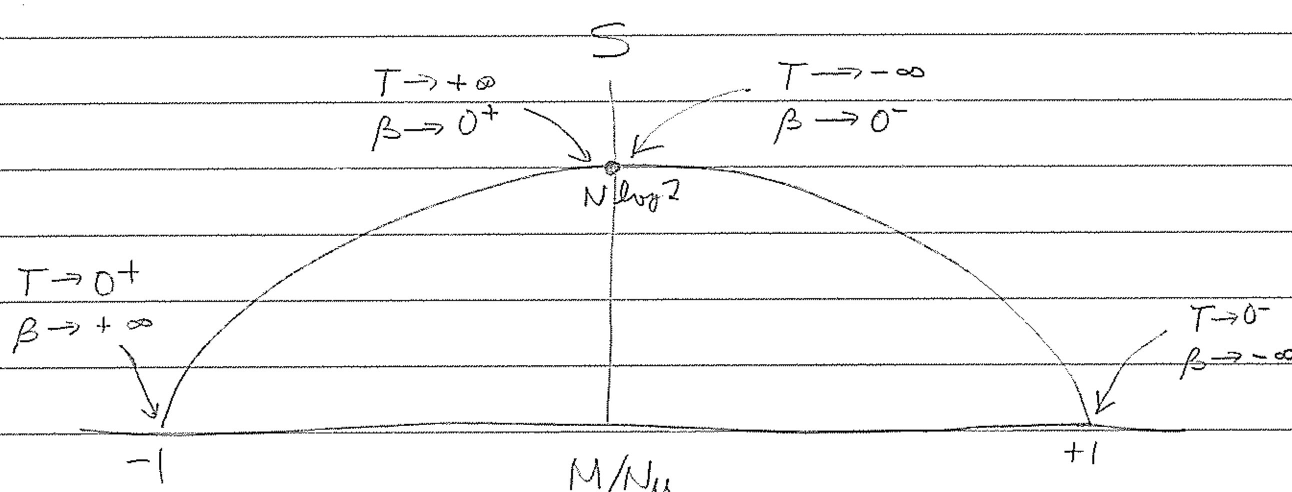
$$= N\mu \frac{e^{\beta\mu B} - e^{-\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}$$

$$= N\mu \frac{e^{2\beta\mu B} - 1}{e^{2\beta\mu B} + 1}$$

$$\Longrightarrow e^{2\beta\mu B} = \frac{N\mu + M}{N\mu - M}$$

$$S = -N\left(\frac{1+M/N\mu}{2}\log\frac{1+M/N\mu}{2} + \frac{1-M/N\mu}{2}\log\frac{1-M/N\mu}{2}\right)$$

Plot S as a function of M



As β decreases continuously from $+\infty$ to 0 to $-\infty$

M increases $-N\mu$ to 0 to $+N\mu$

T increases from 0^+ to $+\infty$

jumps discontinuously to $-\infty$

then increases from $-\infty$ to 0^-

temperature: $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_X = \beta$

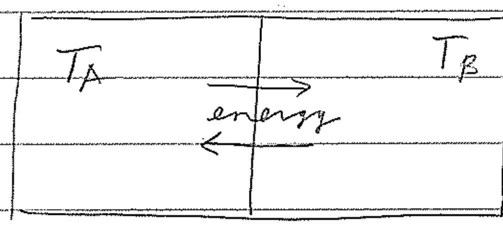
$T > 0 \implies S$ increases as E increases

$T < 0 \implies S$ decreases "

If two systems with different temperature $T_A = \frac{1}{\beta_A}$

$T_B = \frac{1}{\beta_B}$

are brought into thermal contact,



they will eventually reach thermal equilibrium at the same temperature T_{eq}

through a net flow of energy

from system with higher T to system with lower T <u>if</u> T_A and T_B are both positive

from system with lower β to system with higher β