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Thermodynamics and Statistical Mechanics

Statistical Mechanics IV

November 2014

- **Thermodynamics of magnetism**
- **Spin interaction**
- **Second order phase transition**

HYPERBOLIC FUNCTIONS

Hyperbolic functions are defined by

$$\sinh(x) \equiv \frac{e^x - e^{-x}}{2} \quad \cosh(x) \equiv \frac{e^x + e^{-x}}{2} \quad (65)$$

$$\tanh(x) \equiv \frac{\sinh(x)}{\cosh(x)} \quad \coth(x) \equiv \frac{\cosh(x)}{\sinh(x)} = \frac{1}{\tanh(x)} \quad (66)$$

derivatives

$$\sinh(x)' = \cosh(x) \quad \cosh(x)' = \sinh(x) \quad (67)$$

expansions

$$\sinh(x) \cong \begin{cases} x, & x \ll 1 \\ e^x/2, & x \gg 1 \end{cases} \quad \tanh(x) \cong \begin{cases} x, & x \ll 1 \\ 1, & x \gg 1 \end{cases} \quad (68)$$

ELECTRON'S MAGNETIC MOMENT

Angular momentum of point particle in motion $\rightarrow \mathbf{L} = \mathbf{r} \times \mathbf{p} = m\mathbf{r} \times \mathbf{v}$

magnetic moment $\rightarrow \vec{\tau} = \vec{\mu} \times \vec{B}$

vector relating the aligning torque on the object from externally applied \vec{B} -field to the field vector itself

Magnetic moment of point particle in motion $\rightarrow \vec{\mu} = \frac{1}{2}q\mathbf{r} \times \mathbf{v}$

If electron is visualized as classical charged particle rotating about an axis

$$\vec{\mu} = -\frac{e}{2m_e}\mathbf{L}$$

Classical result is off by proportionality factor for spin magnetic moment

$$\vec{\mu} = -g\mu_B \frac{\mathbf{S}}{\hbar}$$

Bohr's magneton $\rightarrow \mu_B = e\hbar/(2m_e) = 9.27 \times 10^{-24} \text{ J/T}$

$$g \simeq 2$$

SPINS IN MAGNETIC FIELD

Magnetism of solids is due to intrinsic angular momentum of electron \rightarrow **spin**

Value of electronic angular momentum $\rightarrow s = 1/2$

eigenvalue of square of electron's angular momentum (in units of \hbar)

$$\hat{s}^2 = s(s + 1) = 3/4$$

Eigenvalues of \hat{s}_z projection $\rightarrow \hat{s}_z = m \quad m = \pm 1/2 \quad (69)$

This results in magnetic moment of electron $\rightarrow \hat{\mu} = g\mu_B\hat{S} \quad (70)$

ZEEMAN HAMILTONIAN

Hamiltonian of electron spin in a magnetic field \mathbf{B} has form

$$\hat{H} = -g\mu_B \hat{\mathbf{S}} \cdot \mathbf{B} \quad (71)$$

minimum of energy corresponds to spin pointing in \mathbf{B} direction

choose z axis in direction of \mathbf{B} $\rightarrow \hat{H} = -g\mu_B \hat{s}_z B$

using (69) energy eigenvalues of electronic spin in magnetic field become

$$\epsilon_m = -g\mu_B mB \quad (72)$$

for electron $m = \pm 1/2$

For atoms spins of all electrons usually combine in collective spin S

that can be greater than $1/2$

(71) becomes $\rightarrow \hat{H} = -g\mu_B \hat{\mathbf{S}} \cdot \mathbf{B}$

Eigenvalues of projections of $\hat{\mathbf{S}}$ on direction of \mathbf{B}

$$m = -S, -S + 1, \dots, S - 1, S$$

altogether $2S + 1$ different energy levels of spin are given by (72)

PARTITION FUNCTION AND FREE ENERGY

Physical quantities of spin are determined by partition function

$$Z_S = \sum_{m=-S}^S e^{-\beta \epsilon_m} = \sum_{m=-S}^S e^{my} \quad \rightarrow \quad y \equiv \beta g \mu_B B = \frac{g \mu_B B}{k_B T} \quad (73)$$

(73) can be reduced to a finite geometrical progression

$$\begin{aligned} (1-x) \sum_{k=0}^n x^k &= (1-x)(x^0 + x^1 + x^2 + \dots + x^n) \\ &= x^0 + x^1 + x^2 + x^3 + \dots + x^n \\ &\quad - x^1 - x^2 - x^3 - \dots - x^n - x^{n+1} \\ &= 1 - x^{n+1} \end{aligned}$$

$$Z_S = e^{-Sy} \sum_{k=0}^{2S} (e^y)^k = e^{-yS} \frac{e^{(2S+1)y} - 1}{e^y - 1} = \frac{e^{(S+1/2)y} - e^{-(S+1/2)y}}{e^{y/2} - e^{-y/2}} = \frac{\sinh[(S+1/2)y]}{\sinh(y/2)} \quad (74)$$

For $S = 1/2$ \rightarrow using $\sinh(2x) = 2 \sinh(x) \cosh(x)$ (74) becomes

$$Z_{1/2} = 2 \cosh(y/2) \quad (75)$$

FREE ENERGY & AVERAGE SPIN POLARIZATION

Partition function being found \rightarrow easily obtain thermodynamic quantities

e.g. \rightarrow free energy \rightarrow

$$F = -Nk_B T \ln Z_S = -Nk_B T \ln \frac{\sinh[(S + 1/2)y]}{\sinh(y/2)}$$

Average spin polarization \rightarrow $\langle S_z \rangle = \langle m \rangle = \frac{1}{Z} \sum_{m=-S}^S m e^{-\beta \epsilon_m}$

using (73) \rightarrow $\langle S_z \rangle = \frac{1}{Z} \frac{\partial Z}{\partial y} = \frac{\partial \ln Z}{\partial y}$

using (67) and (74) \rightarrow $\langle S_z \rangle = b_S(y)$ (76)



$$b_S(y) = \left(S + \frac{1}{2}\right) \coth \left[\left(S + \frac{1}{2}\right) y \right] - \frac{1}{2} \coth \left[\frac{1}{2} y \right]$$

BRILLOUIN FUNCTION

$$b_S(y) = SB_S(Sy)$$

$$B_S(x) = \left(1 + \frac{1}{2S}\right) \coth \left[\left(1 + \frac{1}{2S}\right) x \right] - \frac{1}{2S} \coth \left[\frac{x}{2S} \right]$$

For $S = 1/2$ from (74) $\rightarrow \langle S_z \rangle = B_{1/2}(y) = \frac{1}{2} \tanh \frac{y}{2}$ (77)

$$B_{1/2}(x) = \tanh x$$

$$b_S(\pm \infty) = \pm S \quad \text{and} \quad B_S(\pm \infty) = \pm 1$$

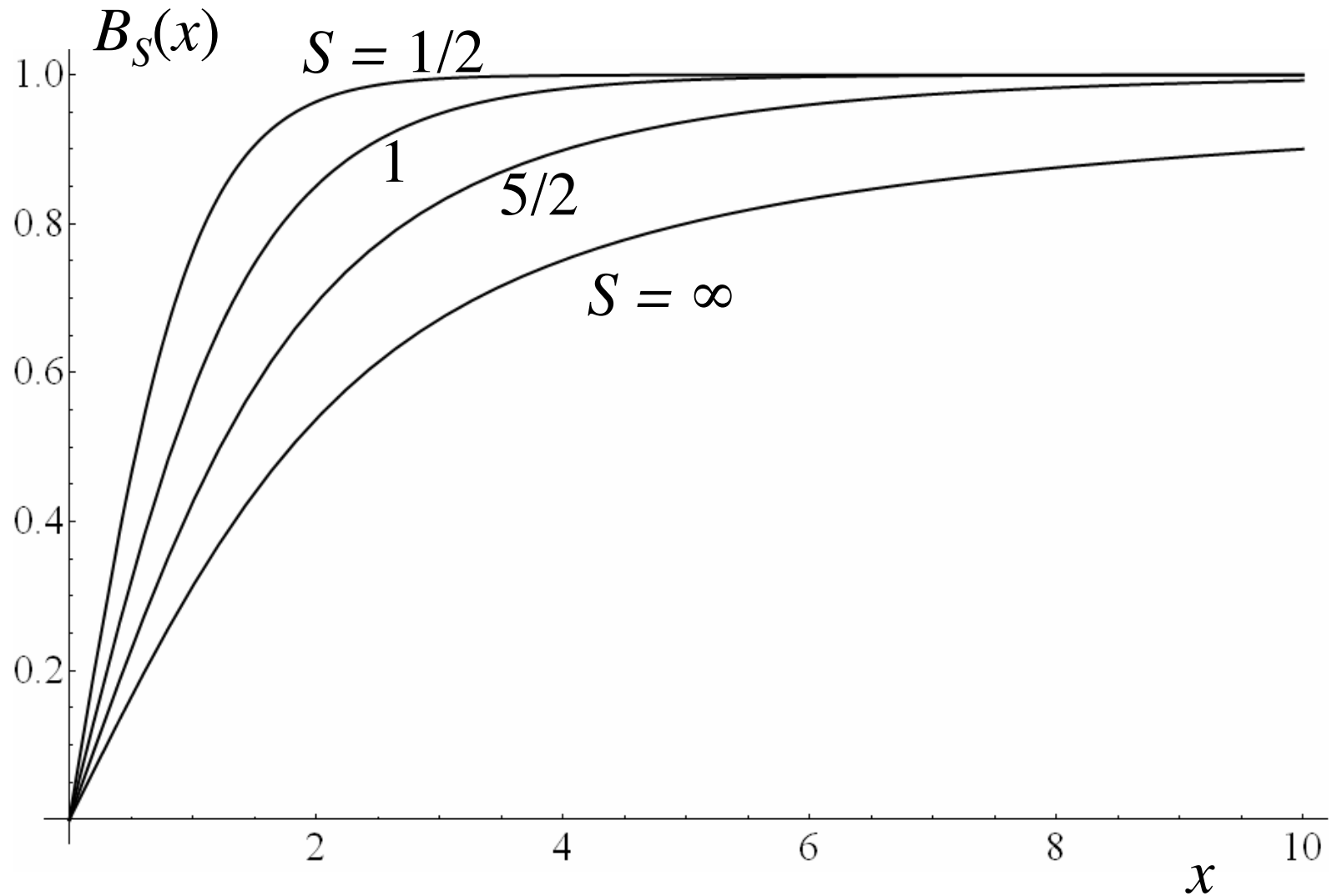
At zero magnetic field $y = 0 \rightarrow$ spin polarization vanishes

This is immediately seen in (77) but not in (76)

to clarify behavior of $b_S(y)$ at small $y \rightarrow$ use $\coth x \cong 1/x + x/3 \rightarrow$

$$\begin{aligned} b_S(y) &\cong \left(S + \frac{1}{2}\right) \left[\frac{1}{\left(S + \frac{1}{2}\right)y} + \left(S + \frac{1}{2}\right) \frac{y}{3} \right] - \frac{1}{2} \left[\frac{1}{\frac{1}{2}y} + \frac{1}{2} \frac{y}{3} \right] \\ &= \frac{y}{3} \left[\left(S + \frac{1}{2}\right)^2 - \left(\frac{1}{2}\right)^2 \right] = \frac{S(S+1)}{3} y \end{aligned} \quad (78)$$

BRILLOUIN FUNCTION $B_S(x)$ FOR VARIOUS S



MAGNETIZATION

In physical units $\rightarrow \langle S_z \rangle \cong \frac{S(S+1)}{3} \frac{g\mu_B B}{k_B T} \quad g\mu_B B \ll k_B T$

Average magnetic moment of spin can be obtained from (70)

$$\langle \mu_z \rangle = g\mu_B \langle S_z \rangle \quad (79)$$

Magnetization of sample M is defined as magnetic moment per unit volume

If there is 1 magnetic atom per unit cell and all of them are uniformly magnetized

$$M = \frac{\langle \mu_z \rangle}{v_0} = \frac{g\mu_B}{v_0} \langle S_z \rangle$$

v_0
unit-cell volume

INTERNAL ENERGY

Internal energy U of a system of N spins

$$U = -N \frac{\partial \ln Z}{\partial \beta}$$

Calculation can be however avoided since from (72) simply follows

$$U = N \langle \varepsilon_m \rangle = -N g \mu_B B \langle m \rangle = -N g \mu_B B \langle S_z \rangle = -N g \mu_B B b_s(y) = -N k_B T y b_S(y) \quad (80)$$

at low magnetic fields (or high temperatures)

$$U \cong -N \frac{S(S+1)}{3} \frac{(g \mu_B B)^2}{k_B T}$$

MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility per spin $\rightarrow \chi = \frac{\partial \langle \mu_z \rangle}{\partial B}$

From (76) and (79) $\rightarrow \chi = \frac{(g\mu_B)^2}{k_B T} b'_S(y)$ (81)

$$b'_S(y) \equiv \frac{db_S(y)}{dy} = - \left(\frac{S + 1/2}{\sinh [(S + 1/2)y]} \right)^2 + \left(\frac{1/2}{\sinh [y/2]} \right)^2$$

For $S = 1/2$ from (76) $\rightarrow b'_{1/2}(y) = \frac{1}{4 \cosh^2 (y/2)}$

From (77) follows $b'_S(0) = S(S + 1)/3$ thus one obtains high-temperature limit

$$\chi = \frac{S(S + 1)}{3} \frac{(g\mu_B)^2}{k_B T} \quad k_B T \gg g\mu_B B$$

In opposite limit $y \gg 1$ function $b'_S(y)$ and thus susceptibility becomes small

Physical reason for this is that at low temperatures $\rightarrow k_B T \ll g\mu_B B$

spins are already strongly aligned by magnetic field $\rightarrow \langle S_z \rangle \cong S$

so that $\langle S_z \rangle$ becomes hardly sensitive to small changes of B

HEAT CAPACITY

Heat capacity C can be obtained from (80) as

$$C = \frac{\partial U}{\partial T} = -N g \mu_B B b'_S(y) \frac{\partial y}{\partial T} = N k_B b'_S(y) y^2 \quad (82)$$

C has a maximum at intermediate temperatures $\rightarrow y \sim 1$

At high temperatures C decreases as $1/T^2$

$$C \cong N k_B \frac{S(S+1)}{3} \left(\frac{g \mu_B B}{k_B T} \right)^2$$

At low temperatures C becomes exponentially small

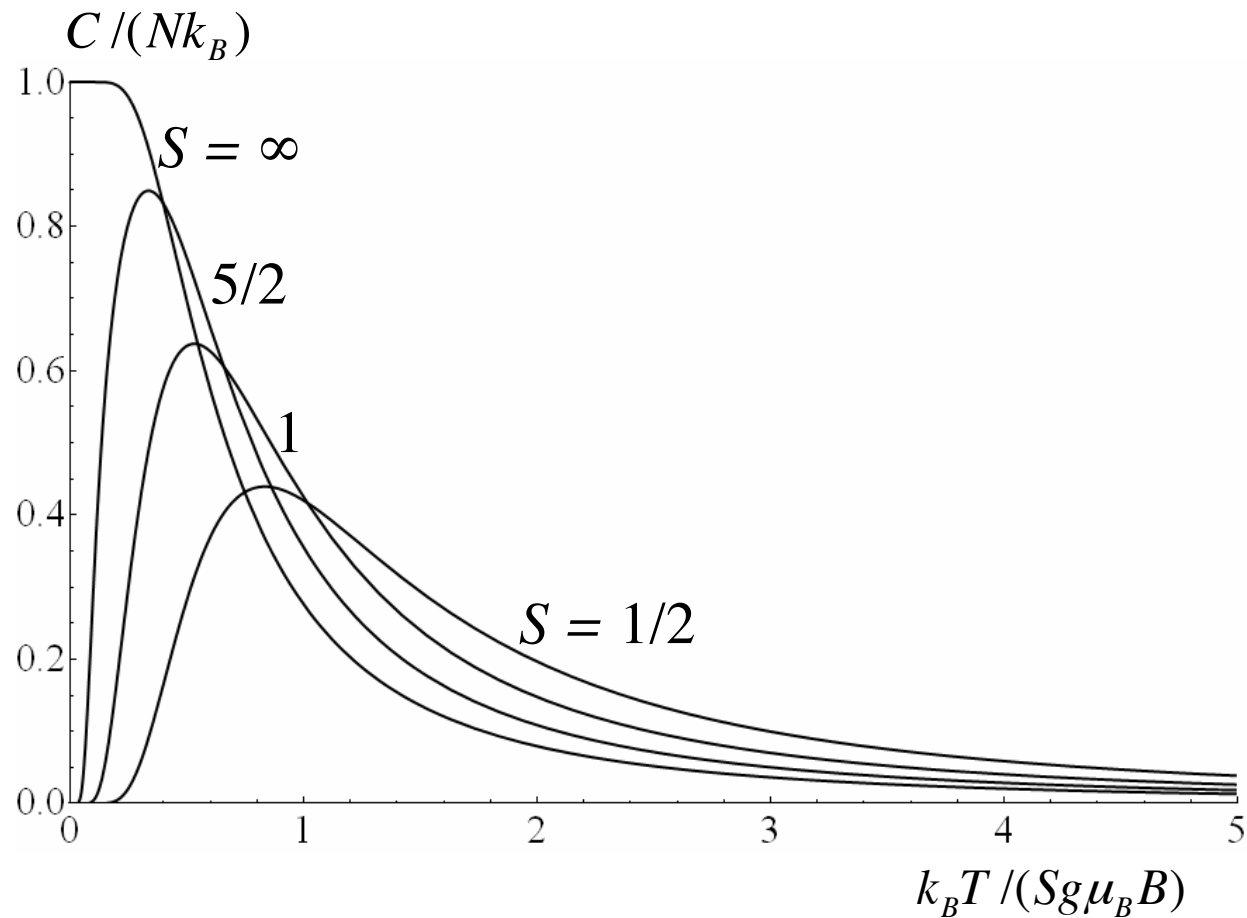
except for case $S = \infty$

(81) and (82) imply a simple relation between χ and C

$$\frac{N \chi}{C} = \frac{T}{B^2}$$

that does not depend on spin value S

TEMPERATURE DEPENDENCE OF HEAT CAPACITY



PHASE TRANSITIONS

We have seen that with changing thermodynamic parameters such as T, P, \dots
system can undergo phase transitions

1st-order phase transitions chemical potentials μ of two competing phases
become equal at phase transition line

while on each side of this line they are unequal

and only one of phases is thermodynamically stable

1st-order transitions are thus abrupt

To contrast \blackleftarrow 2nd-order transitions are gradual:

order parameter continuously grows from zero as phase-transition line is crossed

Thermodynamic quantities are singular at second-order transitions

Phase transitions are complicated phenomena

that arise due to **interaction** between particles

in many-particle systems in thermodynamic limit $N \rightarrow \infty$

SPIN INTERACTION

Simplest forms of interaction between different spins are:

Heisenberg interaction $\rightarrow -J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$

Ising interaction $\rightarrow -J_{ij} \hat{S}_{iz} \hat{S}_{jz}$ including only z components of spins

Exchange interaction $\rightarrow J_{ij}$

follows from quantum mechanical properties of crystal lattice

In most cases there is only interaction J between spins of neighboring atoms
because J_{ij} decreases exponentially with distance

For Ising model \rightarrow all spins in ground state are parallel or antiparallel with z axis
that is \rightarrow it is double-degenerate

For Heisenberg model \rightarrow spins can point in any direction in ground state
so that ground state has a continuous degeneracy

AVERAGE SPIN VALUE AS ORDER PARAMETER

Nature of interaction between spins suggests that at $T \rightarrow 0$
system should fall into its ground state so that
thermodynamic averages of all spins approach their maximal values $|\langle \hat{\mathbf{S}}_i \rangle| \rightarrow S$

With increasing temperature \rightarrow excited levels of system become populated
and average spin value decreases $|\langle \hat{\mathbf{S}}_i \rangle| < S$

At high temperatures \rightarrow all energy levels become populated so that
neighboring spins can have all possible orientations with respect to each other

If there is no external magnetic field acting on spins
average spin value should be exactly zero

because there as many spins pointing in one direction
as there are spins pointing in other direction

This is why high-temperature state is called **symmetric state**

If now temperature is lowered there should be a phase transition temperature T_C
below which order parameter (average spin value) becomes nonzero

Below T_C symmetry of state is spontaneously broken \rightarrow **ordered state**

MEAN-FIELD APPROXIMATION

Idea is to reduce original many-spin problem
to effective self-consistent one-spin problem

by only considering spin i
and replacing other spins in interaction by their average thermodynamic values

$$-J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \Rightarrow -J_{ij} \hat{\mathbf{S}}_i \cdot \langle \hat{\mathbf{S}}_j \rangle$$

Effective one-spin Hamiltonian

$$\hat{H} = -\hat{S} \cdot (g\mu_B \mathbf{B} + Jz \langle \hat{S} \rangle) + \frac{1}{2} Jz \langle \hat{S} \rangle^2$$

z \rightarrow number of nearest neighbors for spin in lattice

$z = 6$ for simple cubic lattice

For Heisenberg model \rightarrow if weak \mathbf{B} -field is applied
ordering will occur in direction of \mathbf{B}

Choosing z axis in this direction

$$\hat{H} = -(g\mu_B B + Jz \langle \hat{S}_z \rangle) \hat{S}_z + \frac{1}{2} Jz \langle \hat{S}_z \rangle^2 \quad (83)$$

Same mean-field \hat{H} is valid for Ising model if B field is applied along z axis

FREE ENERGY PER SPIN

Within MFA Ising and Heisenberg models are equivalent (but not in general!)

Energy levels corresponding to (83) are

$$\varepsilon_m = -(g\mu_B B + Jz\langle\hat{S}_z\rangle)m + \frac{1}{2}Jz\langle\hat{S}_z\rangle^2 \quad m = -S, -S + 1, \dots, S - 1, S$$

Straightforward calculation of partition function (73) leads to free energy per spin

$$F = -k_B T \ln Z = \frac{1}{2}Jz\langle\hat{S}_z\rangle^2 - k_B T \ln \frac{\sinh[(S + 1/2)y]}{\sinh(y/2)}$$
$$y \equiv \frac{g\mu_B B + Jz\langle\hat{S}_z\rangle}{k_B T}$$

To find actual value of order parameter $\langle\hat{S}_z\rangle$ at any T and B

minimize F with respect $\langle\hat{S}_z\rangle$

CURIE-WEISS EQUATION

$$0 = \frac{\partial F}{\partial \langle \hat{S}_z \rangle} = Jz \langle \hat{S}_z \rangle - Jz b_S(y)$$

Rearranging terms one arrives at transcendental Curie-Weiss equation

$$\langle \hat{S}_z \rangle = b_S \left(\frac{g\mu_B B + Jz \langle \hat{S}_z \rangle}{k_B T} \right) \quad (84)$$

For $B = 0$ \rightarrow (84) has only solution $\langle \hat{S}_z \rangle = 0$ at high temperatures

As $b_S(y)$ has maximal slope at $y = 0$

it is sufficient that this slope (with respect to $\langle \hat{S}_z \rangle$) becomes smaller than 1
to exclude any solution other than $\langle \hat{S}_z \rangle = 0$

Using (78) \rightarrow only solution $\langle \hat{S}_z \rangle = 0$ is realized for $T \geq T_C$

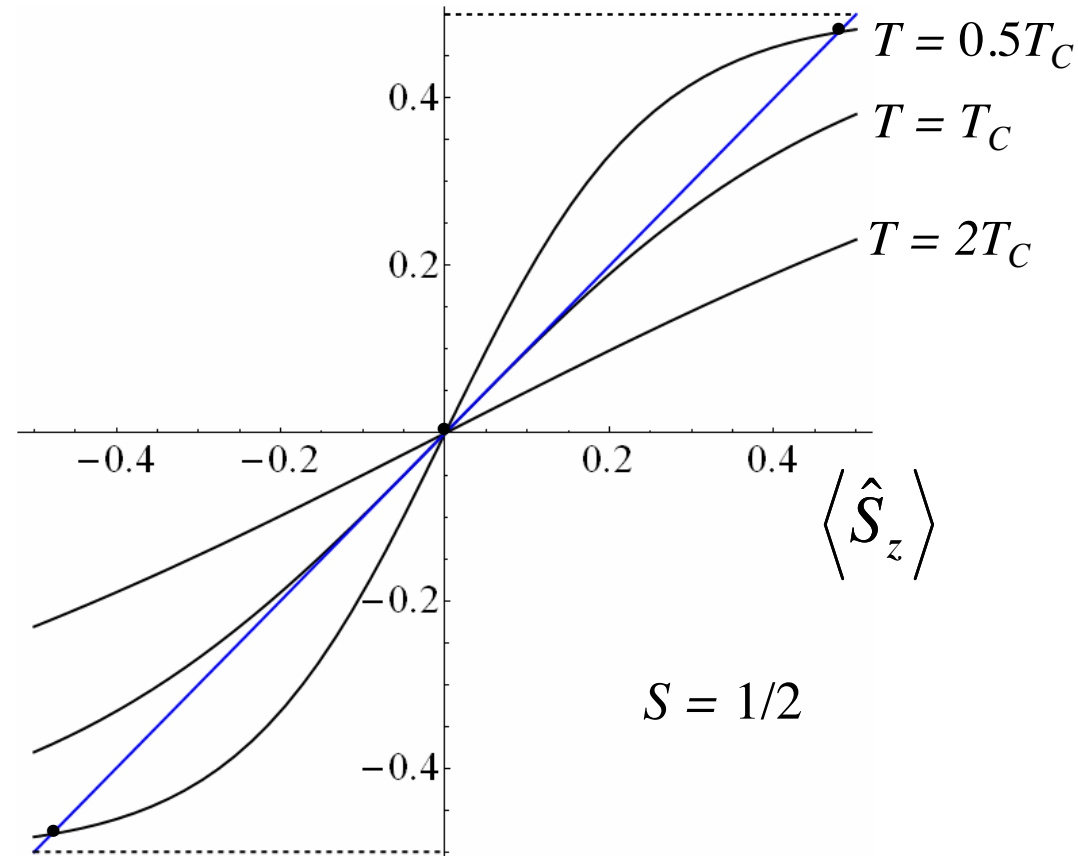
$$T_C = \frac{S(S+1)}{3} \frac{Jz}{k_B} \rightarrow \text{Curie temperature within mean-field approximation}$$

GRAPHIC SOLUTION OF CURIE-WEISS EQUATION

Below T_C slope of $b_S(y)$ with respect to $\langle \hat{S}_z \rangle$ exceeds 1

so that there are three solutions for $\langle \hat{S}_z \rangle$

lhs and rhs of (84)



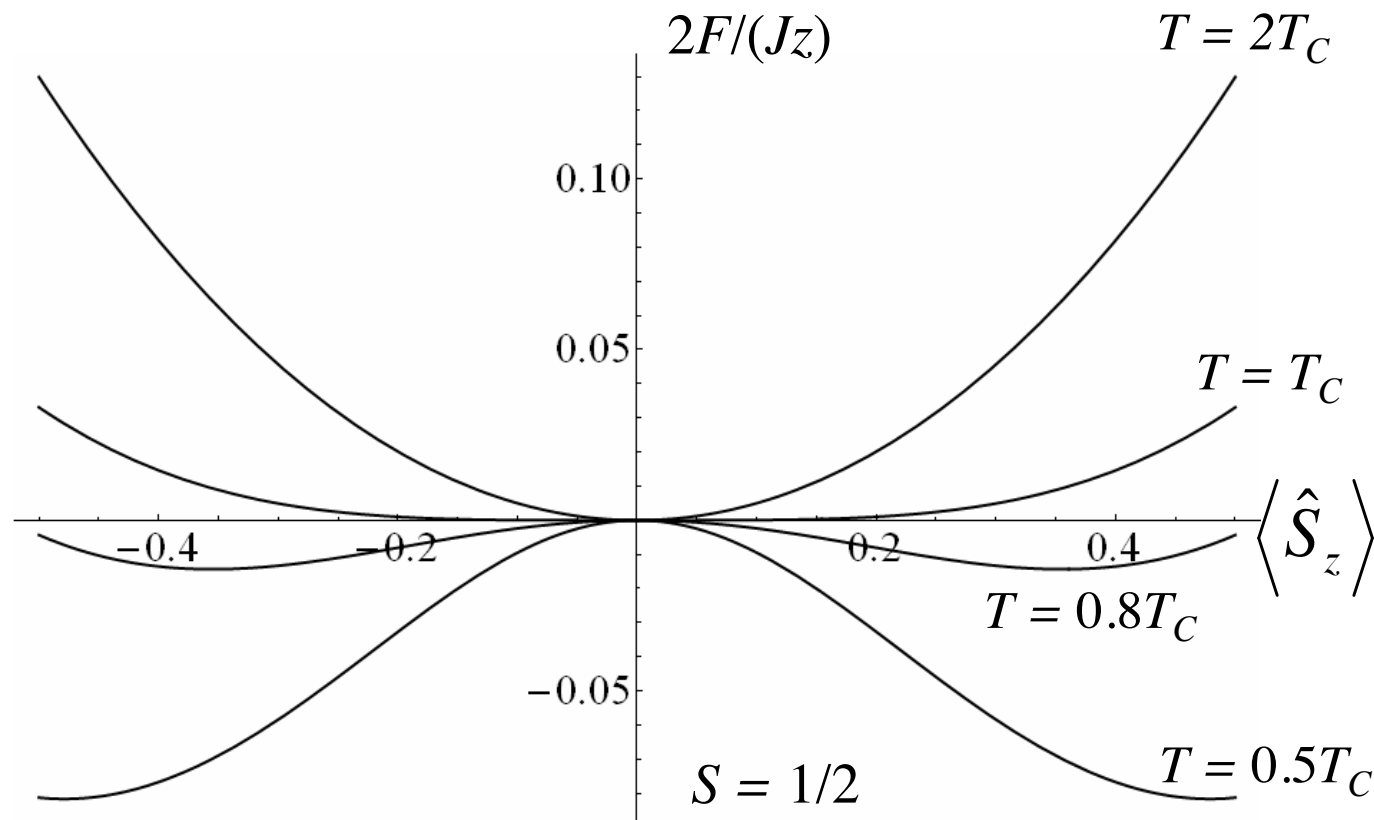
One solution $\langle \hat{S}_z \rangle = 0$ and two symmetric solutions $\langle \hat{S}_z \rangle \neq 0$

FREE ENERGY WITHIN MEAN FIELD APPROXIMATION

solutions $\langle \hat{S}_z \rangle \neq 0$ lower free energy than solution $\langle \hat{S} \rangle = 0$

thus they are thermodynamically stable

These solutions describe ordered state below T_C



(arbitrary vertical shift)