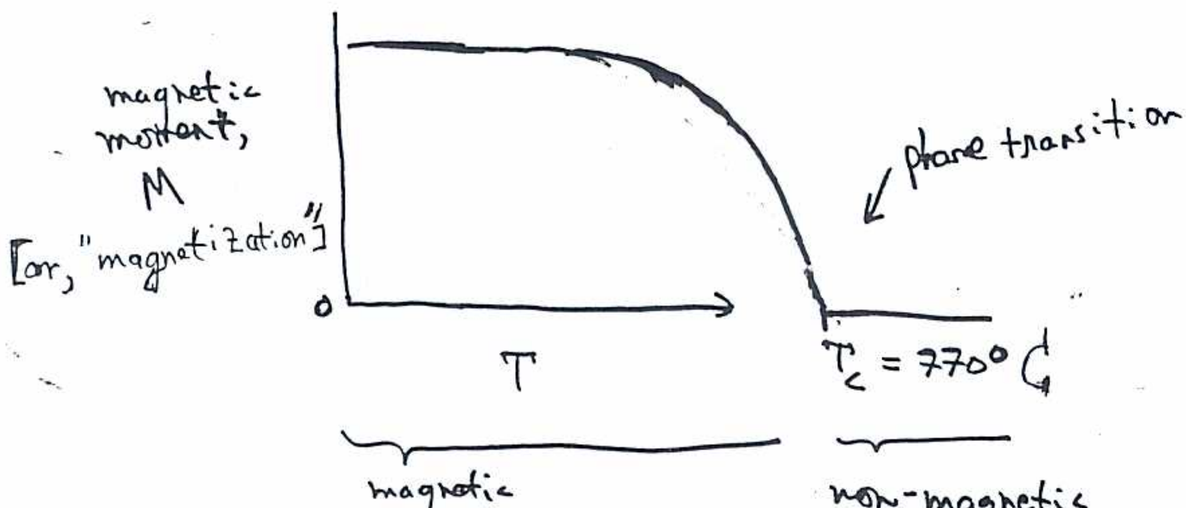
Chem. 1480
Feb 12, 2007

Phase Transitions + Critical Phenomena

Consider Magnetization of IRON



Task: ① explain radical change in properties at T_c via equilibrium statistical mechanics.

② predict quantitatively various equilibrium properties [magnetization, heat capacity, magnetic susceptibility $\left(\frac{\partial M}{\partial H}\right)$], particularly near the critical pt.

E.g., $M \propto (T_c - T)^{\beta}$, $0<\beta<1$ for $T \to T_c^-$

diverge:

$$C_V \propto \begin{cases} (T_c - T)^{-\alpha} & , T \to T_c^- \\ (T - T_c)^{-\alpha'} & , T \to T_c^+ \end{cases} \quad \text{[heat capacity]}$$

$$\left(\frac{\partial M}{\partial H}\right)_{H=0} \equiv \chi_0 \propto \begin{cases} (T_c - T)^{-\gamma} & , T \to T_c^- \\ (T - T_c)^{-\gamma'} & T \to T_c^+ \end{cases} \quad \text{[magnetic susceptibility]}$$

③ Explain why other phase transitions have same critical exponents!
["Universality"]

E.g.: liquid-vapor transition:

	Ferromagnet	Liquid-Vapor
"order parameter" →	M	$\rho_L - \rho_V$
	χ_0	$K_T = \left(\partial \rho_L / \partial P \right)_T$

↑ isothermal compressibility

Equilibrium
Stat. Mech [Boltzmann, Gibbs]: Q = partition fnctn.

$$= \sum_{\substack{k \\ \text{states}}} e^{-\beta E_k} \; ; \; \beta = \frac{1}{kT}$$

All thermodynamic observables can be computed from partition function [vide infra]

[Actually, $\ln Q$ counts]

Ising Model; Illustrate in 2-d

$$\begin{array}{ccccc} \uparrow & \uparrow & \downarrow & \uparrow & \downarrow \\ \downarrow & \uparrow & \uparrow \; J & \downarrow & \downarrow \\ \uparrow & \uparrow & \uparrow & \downarrow & \uparrow \\ \uparrow & \downarrow & \downarrow & \uparrow & \downarrow \end{array}$$

N (= 25 here) spins on [rectangular] lattice; Each spin can be up or down [±1]; 2 kinds of energetic interactions (→)

③

$\big)$, namely

(i) $-\mu H s_j$ $\leftarrow$ "$-\mu \cdot B$" dipole – external field for each spin $\leftarrow$ spin likes to be aligned w/ external field [for $\mu > 0$]

$\mu H = h$

(ii) $-J s_j s_k$ $\leftarrow$ "$\frac{\underset{\sim}{\mu_i} \cdot \underset{\sim}{\mu_j}}{r^3}$" dipole – dipole interaction

J: "ferromagnetic coupling constant"

[NB: a rigorous derivation of the spin-spin coupling constant (including sign) requires quantum mechanics]

↳ [$J > 0$ ferromagnet, neighboring spins favor alignment;
$J < 0$ anti-ferromagnet, neighboring spins favor alternation $\begin{matrix} \uparrow & \downarrow & \uparrow \\ \downarrow & \uparrow & \downarrow \\ \uparrow & \downarrow & \uparrow \end{matrix}$; cf. binary alloys]

NB: Physically (cf. "$\frac{1}{r^3}$"), ferromagnetic interactions assumed short range. In fact, in standard mathematical Ising model, only nearest neighbors couple this way.

Thus,

$$E_C = -J \sum_{\underset{\text{"nearest neighbors"}}{nn}} s_j s_k - h \sum_k s_k$$

↳ "Configuration" = list of state [$\uparrow$ or $\downarrow$] of all N spins

and

$$Q = \sum_C e^{-\beta E_C}$$

Simple illustration ...

1925

1-d Ising Model :

$N = 8$ 2 1

↑ ↓ ↑ ↓ ↑ ↓ ↑ ↑

$$-\beta E_G = \tilde{h}\sum_{k=1}^{N} s_k + \tilde{J}\sum_{k=1}^{N-1} s_k s_{k+1} \quad ; \quad \tilde{h} = \beta h, \ \tilde{J} = \beta J$$

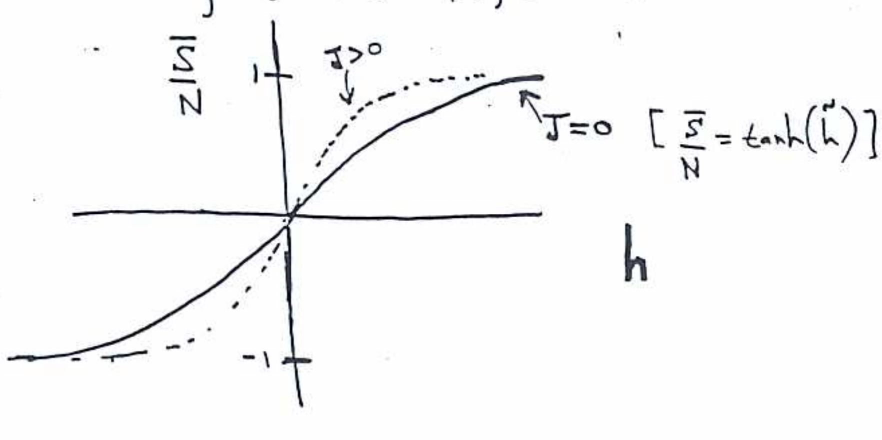
Note: a brute-force summation $\sum_G e^{-\beta E_G}$ involves 2^N terms (!) [$2^{10} \sim 1000$, $2^{20} \sim 10^6$, ⋮ ugh.]

Ising found a way to do the sum analytically; in particular he found that for $N \to \infty$ (thermodynamic limit) ...

$$\frac{\sinh\tilde{h}}{\sqrt{}} = \boxed{\frac{\bar{S}}{N} = \frac{\sinh\tilde{h}\left[1 + \frac{\cosh\tilde{h}}{\sqrt{}}\right]}{\cosh\tilde{h} + \sqrt{}} \ , \quad \sqrt{} = \sqrt{\sinh^2\tilde{h} + e^{-4\tilde{J}}}}$$

1-d ising model

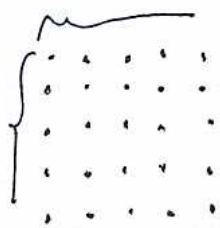
Generic magnetization [fix T, J scan h]:



NB : $\bar{S}(h=0) = 0$, no spontaneous magnetization [for $T > 0$]

i.e. No Phase Transition

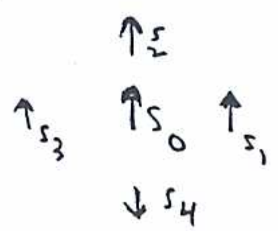
$\mathcal{L} = 5$ (5)

Now, consider 2-D Ising model $\mathcal{L}$  ; for $\mathcal{L} = 10$, # configurations $= 2^{\mathcal{L}^2} = 2^{100} \sim 10^{30}$

Argh! [But cf. Onsager, 1944]

for now, turn to approximation methods...

// **Mean Field Theory** – Simplest version: Each spin moves in an effective h field based on $h_{(ext)}$ + field provided by neighboring spins



To figure (fluctuating w/ $s_1 - s_4$) h_{eff} ; consider energy change when s_0 is flipped w/ neighbors fixed

[Note for spin s_0 (w/ $\mu = 1$) in external field h in ↑ direction
$\Delta E_{flip} = 2h$ to flip s_0 fr. ↑ to ↓]

true external field

$$s_0 \uparrow : \quad E = -h - h\sum_{k=1}^{4} s_k - J \sum_{k=1}^{4} s_k$$

$$s_0 \downarrow : \quad E = h - h\sum_{k=1}^{4} s_k + J \sum_{k=1}^{4} s_k$$

$$\text{so} \quad \Delta E_{flip} = 2h + 2J \sum_{k=1}^{4} s_k \Rightarrow h_{eff} = h + J \sum_{k=1}^{4} s_k$$

$$\xrightarrow{\text{on average}} \boxed{h + \alpha J \bar{s}}$$

average spin / site

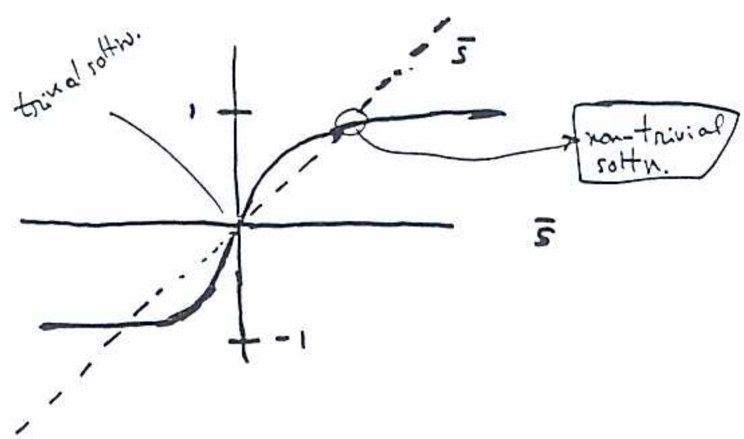
for D-dim. rectangular lattice α = # nearest neighbors = 2D

Thus, using result for $\bar{s}$ for isolated spin in external h field,

$$(*) \quad \boxed{\bar{s} = \tanh\left(\beta\left[h + \alpha J \bar{s}\right]\right)}$$

Mean field, or Self-consistent field Eqn. for $\bar{s}$

Consider soltn. to (*) w/ $h=0$.

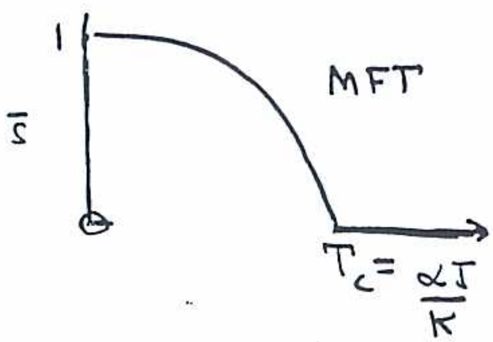


key fact $\tanh x \cong x$ for small x ; $\frac{d}{dx}[\tanh x] = \mathrm{sech}^2 x < 1$

Thus non-zero $\bar{s}$ soltn. to MF Theory $\exists$ iff. $\boxed{\beta \alpha J \geq 1}$

or $\boxed{T \leq \frac{\alpha J}{k}}$

Graphically



} As observed!