Lecture 16 - Phase transitions

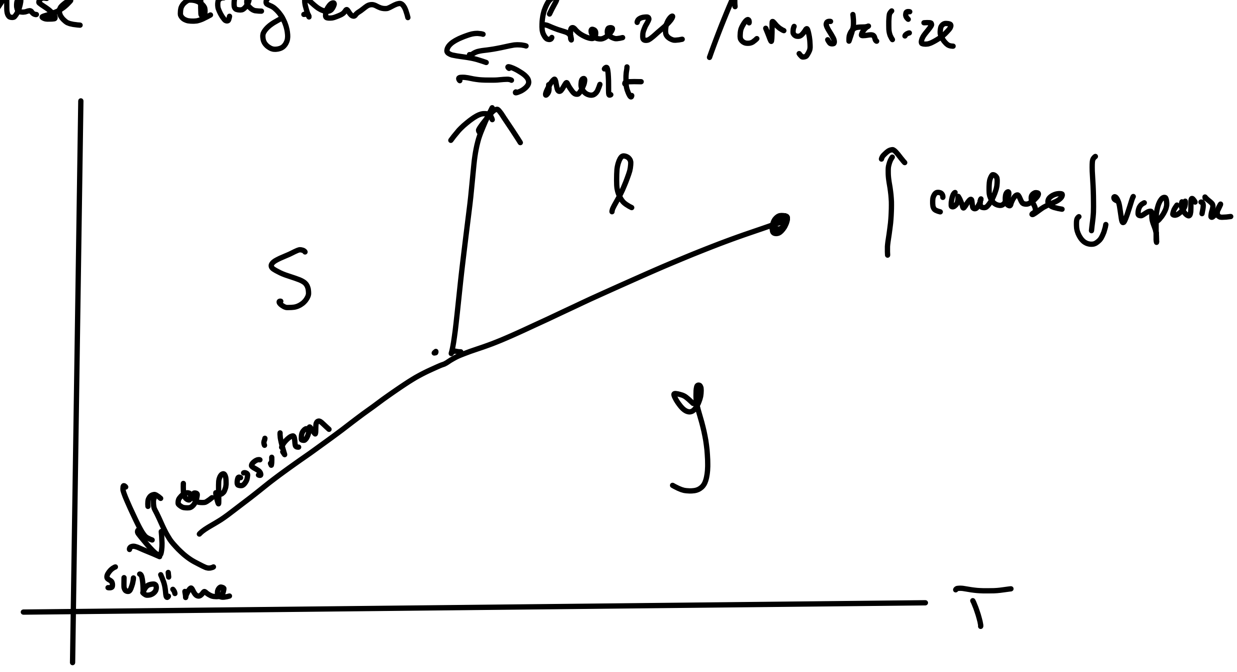
Familiar w/ phase transitions in every day life

In stat mech, we can try to understand

1) Change in macroscopic quantities
   [density, hardness, color, viscosity]
2) Change in microscopic quantities
   [crystal structure, dynamics
3) "Universality" - strange & surprising similarity between seemingly unlike systems

Must start w/ basics and definitions (Ch 16)

Basic phase diagram



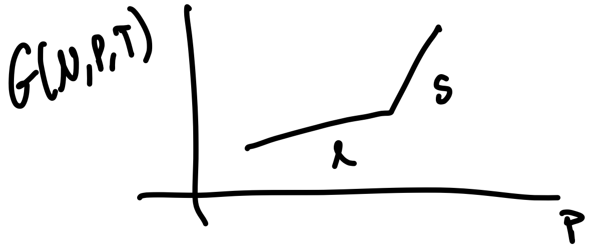
$G(N,P,T) = E - TS + PV$

At a line, free energies are equal

Cross a line, discontinuity in some quantity, for example density

1st order

Ehrenfest definition: discontinuity in <u>1st</u> deriv of the free energy



$$\text{density} = N/V = N/(\partial G/\partial P)$$

Modern definition: latent heat, given off or taken in while two phases coexist

Far right, critical point, go between phases w/o latent heat

@ critical point, 2nd order phase transition

Ehrenfest: cts first deriv, discont second deriv

Modern: "continuous" phase transition,

diverging susceptibility

diverging "correlation length"

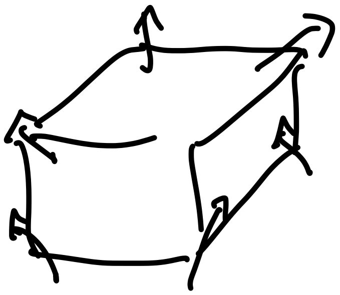
Typically break symmetry

Liq -> solid, translational symmetry broken

Liq -> gas, finite correlation length -> zero correlation length [g(r)]

Model system will help us understand important concepts & which can be solved

Magnetization:



spins on lattice,
like to point same direction

Entropy prevents order

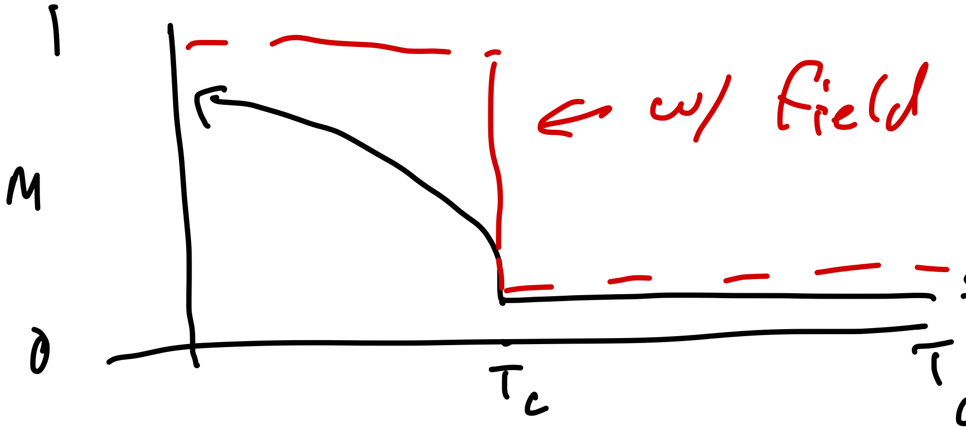
B field causes alignment in direction of the field if "stronger" than entropy

Order parameter for transition ($\rho - \rho_c$ for liq/gas)

$$M = \left|\left\langle \sum_{i=1}^{N} \sigma_i \right\rangle\right| , \quad m = M/N ,$$

the magnetization (per spin)

will see how M is related to a first derivative of free energy



zero field, "spontaneous mag"

cts, but discont slope

Curie temp

for pierre curie, who studied this transition in magnets

Wan't to know when/whether this transition should occur. A bit to complicated to solve, so make an approximate model (also, fully classical)

"Real" Hamiltonian

coupling matrix

$$\hat{H} = -\frac{1}{2}\sum_{ij} \hat{\sigma}_i \cdot J_{ij} \cdot \sigma_j - \sum_i \gamma B \cdot S_i \qquad h = \frac{\gamma \hbar \beta}{2}$$

$$\hat{S}_i = \hbar/2 \, \hat{\sigma}_i \quad \leftarrow \text{Pauli matrix}$$

Consider only z direction & field in z direction

$$H = -\frac{1}{2}\sum_{ij} J_{ij}\sigma_i\sigma_j - \sum_i h\sigma_i \qquad \sigma_i \doteq \{\pm 1/2\}$$

Make short ranged, so only if site i&j adjacent, and approx $J_{ij} = \begin{cases} J & i,j \text{ neigh} \\ 0 & \text{o other} \end{cases}$

redefine regardless of ½, mult by 2

$$\downarrow$$

$$H = -J\sum_{\langle ij\rangle} S_iS_j - \sum_i hS_i \qquad S_i = \{\pm 1\}$$

(Lenz → Ising, 1924) 2d - Onsager 1944

If $J>0$, like to align. $h>0$, like to be "up" w/ $h=0$, min $\mathcal{E}$ when all aligned up or down

Consider config $\langle \uparrow\uparrow\uparrow \cdots \uparrow\uparrow\uparrow \rangle$ $m=1$

or $\downarrow\downarrow\downarrow \cdots \downarrow\downarrow\downarrow$ $m=1$

$\mathcal{E} \approx -NJ$ (boundary effects)

$= \mathcal{E}_{min}$

Now consider $\uparrow\uparrow\uparrow \cdots \uparrow\uparrow\downarrow\downarrow \cdots \downarrow\downarrow\downarrow$ $m=0$

$\mathcal{E} = -NJ + J$

Cost of interface only 1 in N, very small,

so only at $T=0$ get magnetization

In 2d:

$$\begin{array}{cccccccc} \uparrow & \uparrow & \uparrow & \uparrow & \cdots & \uparrow & \uparrow & \uparrow \\ \uparrow & \uparrow & \uparrow & \uparrow & \cdots & \uparrow & \uparrow & \uparrow \\ \downarrow & \downarrow & \downarrow & \downarrow & \cdots & \downarrow & \downarrow & \downarrow \\ \downarrow & \downarrow & \downarrow & \downarrow & \cdots & \downarrow & \downarrow & \downarrow \end{array}$$

$m=0$

$\ell = \sqrt{N}$

$\mathcal{E} = -4NJ + \sqrt{N} J$

This "surface tension" may cost enough to stabilize ordered state at finite but low T

Although 1d ising model doesn't have spontaneous magnetization, many problems like adsorption, protein folding can be mapped to it and so we need to understand it too

Need $Z(N,V,T)$ to get free energy & properties

1d $$\mathcal{H} = -\sum_{i=1}^{N\boxed{-1}} J s_i s_{i+1} - \sum_{i=1}^{N} h s_i$$, can make more symmetrical, can also say $s_{N+1} = s_i$

$$\mathcal{H} = -J \sum_{i=1}^{N} s_i s_{i+1} - \frac{h}{2} \sum_{i=1}^{N} (s_i + s_{i+1})$$

$$= \sum_{i=1}^{N} \left(-J s_i s_{i+1} - \frac{h}{2}(s_i + s_{i+1})\right)$$

$$Z = \sum_{\text{states}} e^{-\beta E(\text{state})} = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} e^{\beta \sum [s_i s_{i+1} - \frac{h}{2}(s_i + s_{i+1})]}$$

for $B = 0$, independent and $Z = \left(\sum_{s_1} e^{\beta h s_i}\right)^N$

$$= \left(e^{-\beta h} + e^{\beta h}\right)^N$$

$$\propto \left(1 + e^{2\beta h}\right)^N$$

like many problems we did before

For $h=0$

$$Z = \sum_{S_1, S_2, S_3, \dots, S_N} e^{\beta J S_1 S_2} e^{\beta J S_2 S_3} \cdots e^{\beta J S_N S_1}$$

Let $\tilde{S}_i = S_i S_{i+1}$, can only be ±1, but 2 ways

If first spin up, we know rest, or down

$$\text{So } Z = 2 \sum_{\tilde{S}_1, \tilde{S}_2, \dots, \tilde{S}_N} e^{\beta J S_1} e^{\beta J S_2} \underbrace{e^{\beta J S_3}}_{ind} \cdots e^{\beta J S_N}$$

$$= 2\left[\sum_{S} e^{\beta J S}\right]^N = 2\left[e^{\beta J} + e^{-\beta J}\right]^N$$

$$= 2\left(2\cosh(\beta J)\right)^N$$

$$A(N,T) = -k_B T \ln Z = -\frac{N}{\beta}\ln(2\cosh(\beta J)) + \text{const}$$

Want to know magnetization vs T at diff β

Lets look back at Z

$$Z = \sum_{\text{states}} e^{+\beta \sum J S_i S_{i+1} + \beta h \sum S_i} , \quad M = \langle \sum S_i \rangle = k_B T \frac{\partial \ln Z}{\partial h} \; !$$

To calculate this at $h=0$, need to compute M for finite h and then take $h \to 0$

To do this, need a new technique called transfer matrices

Reminder $A = \begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}$ $B = \begin{pmatrix} b_1 & b_2 \\ b_3 & b_4 \end{pmatrix}$

$$AB = \begin{pmatrix} a_1 b_1 + a_2 b_3 & a_1 b_2 + a_2 b_4 \\ a_3 b_1 + a_4 b_3 & a_3 b_1 + a_4 b_4 \end{pmatrix}$$

Define $P_{s,s'}$ as the matrix w/ entries

$$e^{\beta J s s' + \beta h (s+s')/2}$$

Then evaluate for 4 cases $1,1$ $\quad 1,-1$

$-1,1$ $\quad -1,-1$

$$P = \begin{pmatrix} e^{\beta(J+h)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} \end{pmatrix}$$

$P_{s_i s_{i+1}}$

Remember

$$Z = \sum_{\{s_i\}} e^{\beta J (s_i s_{i+1}) + \beta h/2 (s_i + s_{i+1})}$$

sum over all possible combinations

analagously to QM bra-ket, write

$$|1\rangle = \begin{pmatrix}1\\0\end{pmatrix} \qquad |-1\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$

$$\langle 1| = (1\ 0) \qquad \langle -1| = (0\ 1)$$

Then $P_{ss'} = \langle s|P|s'\rangle$

and $Z = \sum_{\{S_i\}} \langle S_i|P|S_{i+1}\rangle$

b/c $\sum_{S_i} |S_i\rangle\langle S_i| = \begin{pmatrix}1&0\\0&0\end{pmatrix} + \begin{pmatrix}0&0\\0&1\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix} = I_2$

this means $Z = \sum_{S_1} \langle S_1|P\cdot P\cdot P\cdots P|\overset{S_{N+1}}{\overset{\shortparallel}{S_1}}\rangle$

$$= \sum_{S_1} \langle S_1|P^N|S_1\rangle = Tr(P^N)$$

$$= Tr(UD^NU^{-1}) = Tr(D^N) = \sum_{i=1}^{N} \lambda_i^N$$ for λ_i eigenvals of P!

so $Z = \lambda_1^N + \lambda_2^N$

$Det[P - \lambda I] = 0$ solutions

$$= \begin{vmatrix} e^{\beta(J+h)} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-h)} - \lambda \end{vmatrix} = (e^{\beta(J+h)} - \lambda)(e^{\beta(J-h)} - \lambda) - e^{-2\beta J}$$

$$= \lambda^2 - \lambda(e^{\beta(J+h)} + e^{\beta(J-h)}) + e^{2\beta J} - e^{-2\beta J}$$

$$= \lambda^2 - 2\lambda e^{\beta J}\cosh(\beta h) + 2\cosh(2\beta J)$$

$$\lambda_{\pm} = e^{\beta J}\cosh(\beta h) \pm \sqrt{e^{2\beta J}\cosh^2(\beta h) - e^{2\beta J} - e^{-2\beta J}}$$

$$\lambda_{\pm} = e^{\beta J}\cosh(\beta h) \pm \sqrt{e^{2\beta J}[1+\sinh^2(\beta h)] - e^{2\beta J} - e^{-2\beta J}}$$

$$= e^{\beta J}\cosh(\beta h) \pm \sqrt{e^{2\beta J}\sinh^2(\beta h) - e^{-2\beta J}} \quad ☆$$

$$= e^{\beta J}\left[\cosh(\beta h) \pm \sqrt{\sinh(\beta h) - e^{-4\beta J}}\ \right]$$

$\lambda_+ > \lambda_-$ so as $N \to \infty$

$$Z \to \lambda_+^N$$

Hence $F(N, V, T, h) \approx -\frac{N}{\beta}\ln[\lambda_+]$

or $f(h, \beta) \approx -\frac{1}{\beta}\ln[\lambda_+]$

$$m(h,\beta) = k_BT\frac{\partial \ln Z}{\partial h} \approx k_BT\frac{\partial \ln \lambda_+}{\partial h}$$

$$= \frac{\sinh(\beta h) + \frac{1}{2}\left(\sinh^2(\beta h) - e^{-2\beta J}\right)^{-1/2} \cdot 2\sinh(\beta h)\cosh\beta h}{\cosh(\beta h) + \sqrt{\sinh^2(\beta h) - e^{-2\beta J}}}$$

as $h \to 0$ $\quad \cosh = \frac{1}{2}(e^+ + e^-) \to 1$

$\quad\quad\quad\quad\ \sinh = 1/2(e^+ - e^-) \to 0$

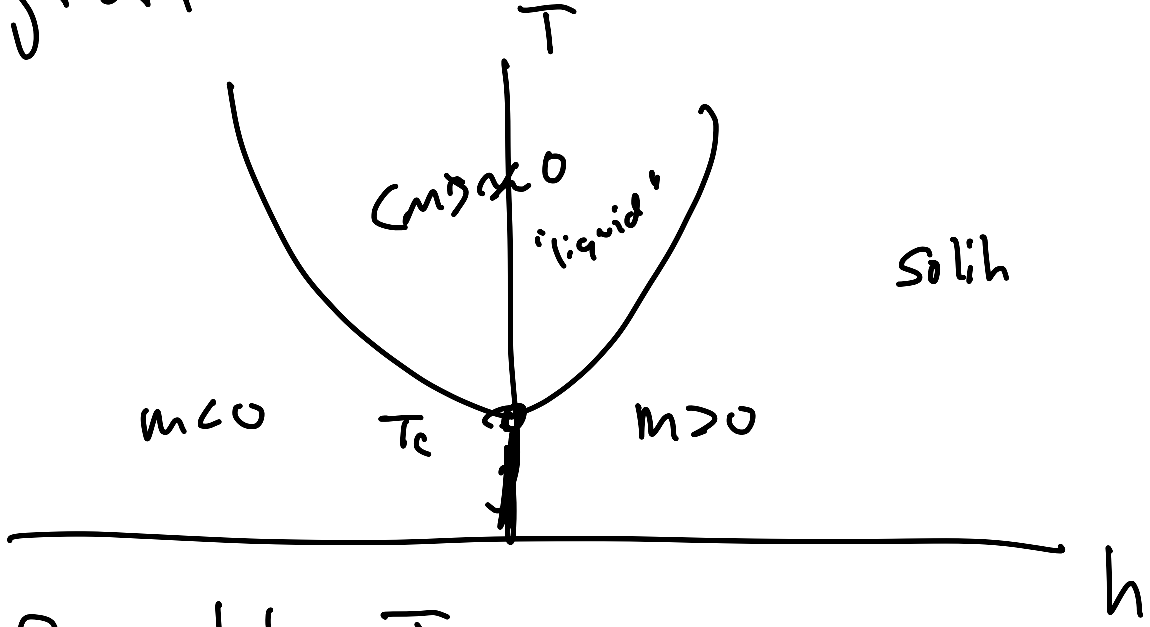
So $\lim_{h \to 0} m(h,\beta) = 0$ if $\beta < \infty$ $(T > 0)$

as $\beta \to \infty$ $\quad e^{-2\beta J} \to 0$ first leaving

$$\frac{\sinh(\beta h) \pm}{\cosh(\beta h) \pm} \frac{\cosh\beta h}{\sinh(\beta h)} \to \pm 1$$

depending on $h > 0$ or $h < 0$ to start

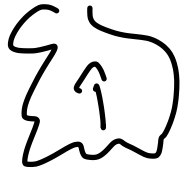
Phase diagram
for n-d



for 1d, T = 0

What about higher dimensions?
Can we solve approximately?

Mean field theory: imagine each spin feels average spin of neighbors, which is m! × z, # neigh (2·d)



Call $\delta s_i = s_i - m \Rightarrow s_i = m + \delta s_i$

$$H = -\frac{J}{2}\sum_{\langle ij\rangle}(m+\delta s_i)(m+\delta s_j) - h\sum_i s_i$$

$$\approx -J/2 \sum_{\langle ij\rangle}\left(m^2 + \overset{m(s_i+s_j)-2m^2}{m(\delta s_i+\delta s_j)} + \overset{\text{small}}{\cancelto{0}{\delta s_i \delta s_j}}\right) - h\sum_i s_i$$

$$= Jm^2Nz - m\frac{J}{2}\sum_{\langle ij\rangle}(S_i+S_j) - h\sum_i S_i$$

$$= Jm^2Nz - (h+2mJz)\sum_{i=1}^{N} S_i$$

$$Z = \sum_{S_1}\sum_{S_2}\cdots\sum_{S_N} e^{-\beta[\;\downarrow\;]}$$

$$= e^{-\beta Jm^2Nz}\cdot\left[\sum_S e^{\beta(h+2mJz)S}\right]^N$$

$$= e^{-\beta Jm^2Nz}\cdot\left[2\cosh(\beta(h+2mJz))\right]^N$$

$$m = \frac{k_BT}{N}\frac{\partial \ln Z}{\partial h} = k_BT\frac{\partial}{\partial h}\left[\ln(2\cosh(\beta(h+2mJz)))\right]$$

$$= k_BT\,\frac{2\sinh(\beta(h+2mJz))\cdot\beta}{2\cosh(\beta(h+2mJz))}$$

$$= \tanh(\beta(h+2mJz))$$

no analytical solution, can get numerically

Is there a transition? $h=0$

So 2 solutions for $2\beta J z > 1$

ie $k_BT < 2Jz$

predict $k_BT_c = 2Jz$

This is ~~qualitata~~qualitatively wrong in 1d, ok in 2d, more accurate as $d \to \infty$

Can also expand the free energy at zero field

$$Z = e^{-\beta J m^2 N z} \cdot \left[2\cosh(\beta(h + 2mJz)) \right]^N$$

$$f = -\frac{k_B T}{N} \ln Z = Jm^2 z - k_B T \ln\left[2\cosh(\beta 2 m J z)\right]$$

close to T_c, $m=0$ so what is free energy in this area

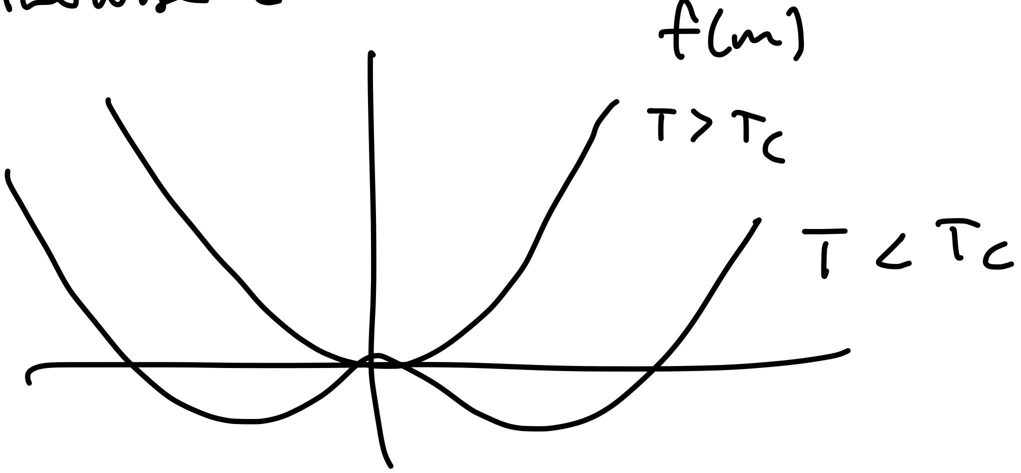
$\ln(\cosh(x)) \approx x^2/2 - x^4/12$

$$f \approx -k_B T \ln 2 - \frac{k_B T}{2}(2\beta m J z)^2 + \frac{k_B T}{12}(2\beta m J z)^4 + Jm^2 z$$

Quartic, either

for $2\beta J z < 1$, f has only 1 min

otherwise 2



Vanish of 2 stable states leads to continuous phase transition