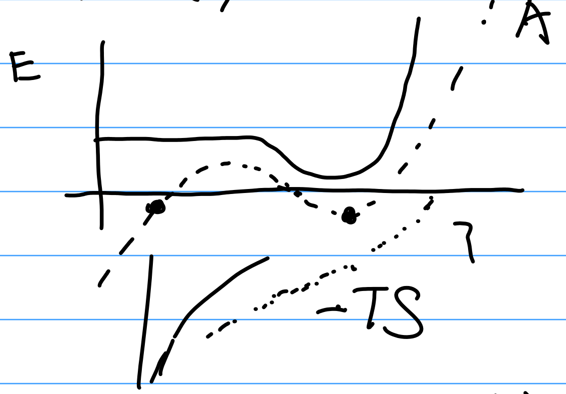
Minimize Free energy:

$$A = E - TS$$

consider an order parameter, ζ

$$A = E(\zeta) - TS(\zeta)$$

An example of $E(\zeta)$:



two ζ giving the same minimum A.

Review: Classical gas, non interacting

$$Q = \frac{1}{N!} q_1^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3} q_{int}\right)^N$$

$$A = -k_B T \ln Q = N k_B T \ln\left(\frac{\rho \lambda_{th}^3}{q_{int}}\right) - N k_B T$$

For phase transition, chemical potential stays same.

Use Gibbs-Free energy:

$$G = \mu N = A + pV$$

$$= A + N k_B T$$

$$G = N k_B T \ln\left(\frac{\rho \lambda_{th}^3}{q_{int}}\right)$$

Now do mean-field theory:

$$A(N, T, V) \to A(N, T, \underbrace{V - Nb}_{\text{excluded volume.}}) + \underbrace{E_{MF}}_{\text{Mean-Field.}}$$

$$E_{MF} \propto \rho^2 V = N\rho$$

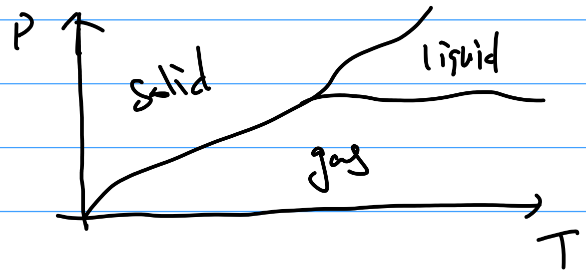
$$\boxed{E_{MF} = -N\rho a}$$

$$\boxed{\begin{aligned} A &= N\left[k_B T \ln\left(\frac{\rho \lambda_{th}^3}{q_{int}}\right) - k_B T - \rho a\right] \\ p &= -\rho^2 a + \rho \frac{k_B T}{1 - \rho b} \end{aligned}}$$

For van-der-Waals gas

$$\boxed{\mu = \frac{G}{N} = \frac{A + pV}{N} \Rightarrow \mu = k_B T \ln\left(\frac{\rho \lambda_{th}^3}{1 - \rho b}\right) - 2\rho a + k_B T \frac{\rho b}{1 - \rho b}}$$

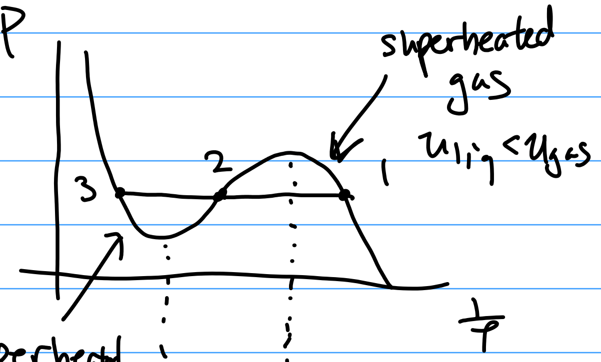
This phase transition has a latent heat:



Heating but stays at constant temp.

To find the latent heat:

$$\frac{dP_0}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{L}{T\Delta V}$$



$$\int_1^3 dG = 0$$

$$\int_1^3 \cancel{-SdT} + Vdp + \cancel{udN} = 0$$

$$\int_1^3 dV(p - p_0(T)) = 0$$

Superheated liquid

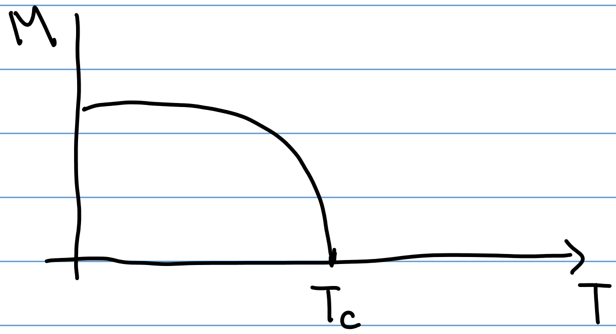
$u_{liq} > u_{gas}$

metastable

unstable, so it goes through line rather than curve.

Continuous Phase Transition: No latent heat.

1st order Phase Transition: Has Latent heat



$$\partial A = -S\,dT - m\,dH$$

$$\langle M \rangle = -\frac{\partial A}{\partial H} = \text{continuous}$$

applied field

$$\chi = \frac{\partial \langle m \rangle}{\partial H} = -\left(\frac{\partial^2 A}{\partial H^2}\right)_{N,T} \xrightarrow{T=T_c} \infty$$

Near critical point

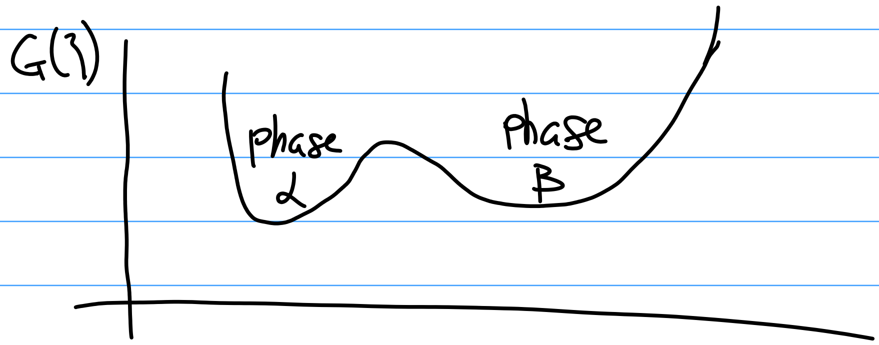
$$\frac{\partial M}{\partial H} = \chi \propto \frac{1}{\left(1-\frac{T}{T_c}\right)^{\gamma}} = \frac{1}{\tau^{\gamma}} \qquad \gamma \cong 1.3$$

$$C \propto \frac{1}{\left(1-\frac{T}{T_c}\right)^{\alpha}} \qquad \alpha \cong \frac{1}{8}$$

$$\eta \propto \tau^{\beta} \qquad \beta \approx \frac{1}{3}$$

$$\alpha + 2\beta + \gamma = 2$$

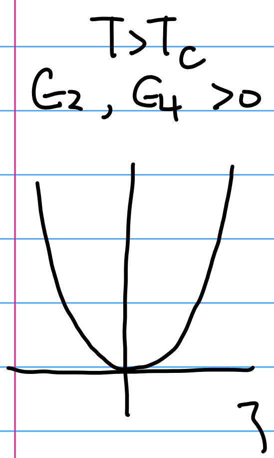
Landau Theory:

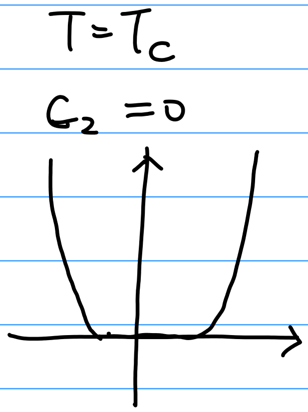


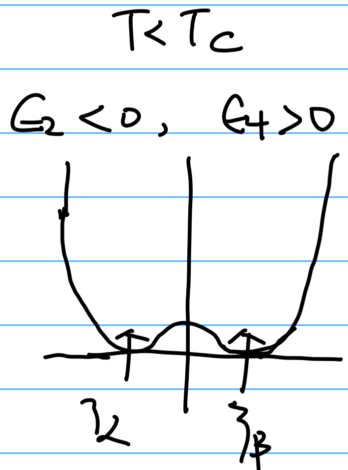
Near critical point:

$$G(\xi) = G_0 + G_2 \xi^2 + G_4 \xi^4$$

depend on T







symmetry breaking

External Field: $G \to G - \mu H\langle m \rangle$

applied field

$$g = \frac{G}{N} \Rightarrow \Delta g = \frac{G-G_0}{N} = -a\tau\xi^2 + \frac{1}{2}b\xi^4 - ph\xi + f(|\vec{\nabla}\xi|^2)$$

$\tau = 1 - \frac{T}{T_c}$

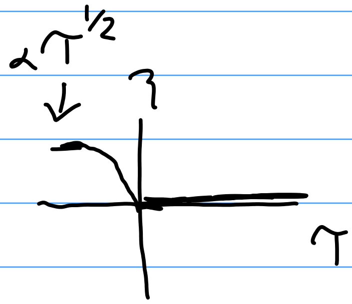
$h \simeq \mu H$ → magnetic field

$f(|\vec{\nabla}\xi|^2)$ → kinetic

Take $h=0$, $f=0$

$$\frac{\partial g}{\partial \xi} = 0 = -2a\tau\xi + 2b\xi^3$$

For $T < T_c$: $\xi = \left(\frac{a\tau}{b}\right)^{1/2}$



Since $\tau = 0$ for $T > T_c$

$T > T_c$: $\xi = 0$

Since $\xi \propto \tau^{\beta}$

$\boxed{\text{Find } \beta = \frac{1}{2}}$

<u>If $h \neq 0$</u>:

ignore higher order.

$$\frac{\partial g}{\partial \xi} = 0 = -2a\tau\xi + \cancel{2b\xi^3} - ph$$

$$\xi = \frac{-ph}{2a\tau}$$

Since $\chi \propto \frac{1}{\tau^{\gamma}}$ Find $\gamma = 1$

Ising Model:

⇒ Each particle is fixed on a lattice. (No Motion)

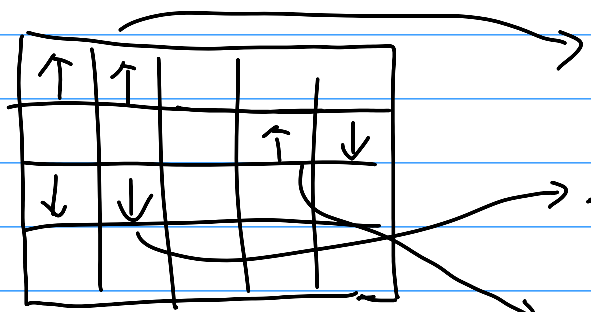
⇒ Each lattice can only be in one of two states. ↑↓

⇒ Each spin only interacts (parwise) with nearest neighbor.

$$\mathcal{H} = -J \sum_{\substack{(ij) \\ \text{pair}}} S_i S_j - \sum_{i=1}^{N} H u S_i$$

$S_{ij} = \pm 1$, classical spin

J = Interaction Strength
H = external field
u = Magnetic moment



$-J(1)(1) = -J$

$-J(-1)(-1) = -J$

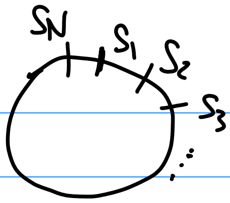
} lower energy

$-J(-1)(1) = +J$ ⇒ Higher Energy

$$Q(N, \beta, H) = \sum_{S_1=\pm1} \cdots\cdots \sum_{S_N=\pm1} \exp\{\underbrace{\beta u H}_{\equiv h} \sum S_i + \underbrace{\beta J}_{\equiv K} \sum_{\substack{ij \\ \text{pair}}} S_i S_j\}$$

For 1D: $\sum_{ij} S_i S_j \Rightarrow \sum_i S_i S_{i+1}$

Consider 1D model:



$$Q = \sum_{S_1=\pm1} \cdots \sum_{S_N=\pm1} \exp\left[K S_i S_{i+1} + \tfrac{1}{2}h(S_i + S_{i+1})\right]$$

4 possibilities in the end.

If $S_i = 1$, $S_{i+1} = 1$, $Q \propto e^{K+h}$

If $S_i = -1$, $S_{i+1} = 1$, $Q \propto e^{-K}$

If $S_i = 1$, $S_{i+1} = -1$, $Q \propto e^{K}$

If $S_i = -1$, $S_{i+1} = -1$, $Q \propto e^{K-h}$

Transfer Matrix:

$$P_{i,j} = \begin{array}{cc} (1,1) & (-1,1) \\ \multicolumn{2}{c}{\begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix}} \\ (-1,1) & (-1,-1) \end{array}$$

$$Q = \sum_{S_1=\pm1} \cdots \sum_{S_N=\pm1} \underbrace{\langle S_1|\hat{P}|S_2\rangle\langle S_2|\hat{P}|S_3\rangle \cdots \langle S_{N-1}|\hat{P}|S_N\rangle\langle S_N|\hat{P}|S_1\rangle}_{\text{Diagonal}}$$

$$\mathrm{Tr}\left([P]^N\right) = \lambda_1^N + \lambda_2^N$$

Get : $\lambda = e^{K}\cosh(h) \pm \left[e^{-2K} + e^{2K}\sinh^2(h)\right]^{1/2}$

For $N \gg 1$,

then just consider the larger λ, for λ^N:

If $\lambda_+ \gg \lambda_-$, then

$$Q \approx \lambda_1^N$$

$$\frac{1}{N}\ln Q = \ln \lambda_1$$

$$= \ln\left[e^{K}\cosh(h) + \left(e^{-2K} + e^{2K}\sinh^2(h)\right)^{1/2}\right]$$

$$A = -NJ - Nk_BT\ln\left[\cosh(h) + \left(e^{-4K} + \sinh^2(h)\right)^{1/2}\right]$$

<u>For $h=0$:</u>

$$Q = \left(2\cosh(K)\right)^N$$

$$A = -Nk_BT\ln\left(2\cosh(K)\right)$$

$$\langle M \rangle = -\left(\frac{\partial A}{\partial H}\right)_T$$

$$dE = TdS - MdH$$
$$dA = -SdT - MdH$$

then

$$\langle M \rangle = \frac{N\mu\sinh(h)}{\left[e^{-4K} + \sinh^2(h)\right]^{1/2}}$$

Spontaneous Magnetization

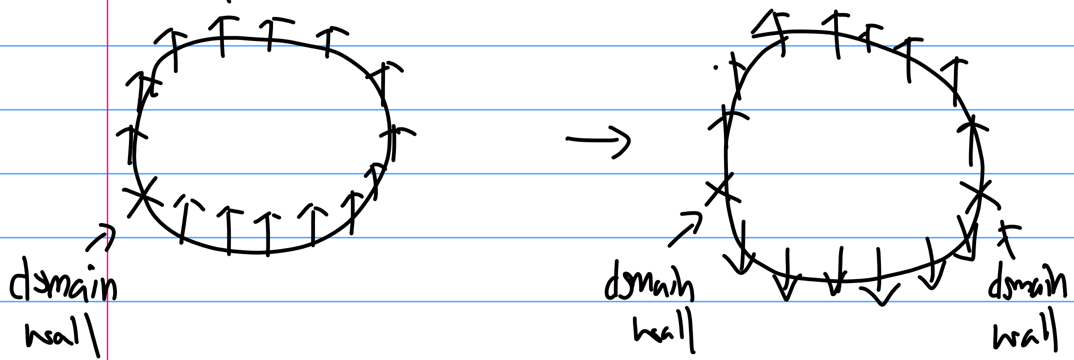
<u>$M(H=0, T)$</u>

as $\lim_{h \to 0} \dfrac{N\mu\sinh(h)}{e^{-2K}} \to 0$ unless $T \to 0$,

so no phase transition at finite T.

If $J=0$: $\langle M \rangle = N\mu \tanh(\beta \mu H)$

No phase transition, why?:



$$\Delta E = 2J + 2J$$

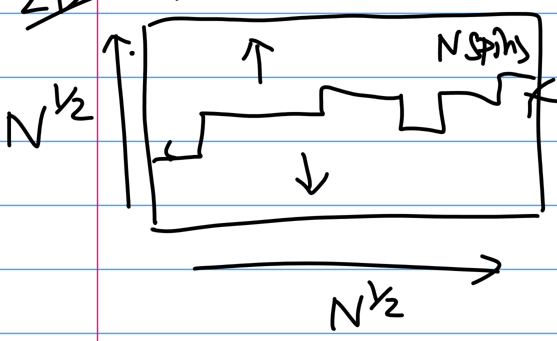
choice of putting wall

$$\Delta S = k_B \ln(N(N-1))$$

$$\Delta A = \Delta E - T\Delta S$$
$$= 4J - 2k_B T \ln N$$

For $\Delta A > 0$, $T_c = \dfrac{2J}{k_B \ln N} \xrightarrow{\text{as } N\to\infty} 0$

2D: peierl's Argument:



domain wall has strength (Length) $L \sim N^{1/2}$

$\Delta E = 2JL$, 2 spin neighboring wall.

$2N^{1/2}$ starting point, 3 choice after.

$\Omega \sim 2N^{1/2} 3^L$

$L \propto N^{1/2}$

$$\Delta A = 2JL - k_BT \ln\left(2N^{1/2}\, 3^L\right)$$

$$\approx \underbrace{2JL}_{N^{1/2}} - \underbrace{k_BTL\ln(3)}_{N^{1/2}} - \cancel{\frac{1}{2}k_BT\ln(N)} - \cancel{k_BT\ln 2}$$

For $N \gg 1$

$\underline{\Delta A = 0}$

$$T_c \approx \frac{2J}{k_B \ln 3} = \frac{J}{k_B}(1.82)$$

exact: $T_c = 2.269\, J/k_B$

going above: disorder
going below: ordered

Exact Solutions for 2D:

$$Q = \left[2\cosh(\beta J)\, e^{I}\right]^N$$

$$I = \frac{1}{2\pi}\int_0^{\pi} d\phi\, \ln\left(\frac{1}{2}\left[1 + (1 - k^2\sin^2\phi)\right]\right), \quad k = \frac{2\sinh(2\beta J)}{\cosh^2(2\beta J)}$$

$$\frac{C}{N} \sim \frac{8k_B}{\pi}(\beta J)^2 \ln\left|\frac{1}{1 - T/T_c}\right|$$

$$m \propto \left|1 - T/T_c\right|^{1/8}$$

Correlation Function:

ensemble average

$$g(r) = \langle S_k S_{k+r} \rangle \sim e^{-r/\xi}$$

correlation length.

$$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow \downarrow$$

$k \qquad\qquad k+r$

→ Higher Temp → more disorder → shorter correlation length.

→ lower Temp → less disorder → longer correlation length

For $r=1$: Nearest Neighbor Interaction:

$H=0$:

trick $J \to J_i$

$$Q = \sum_{S_1=\pm1} \cdots \sum_{S_N=\pm1} \exp\{\beta J_i S_i S_{i+1}\}$$

$$= \sum_{S_1=\pm1} \cdots \sum_{S_N=\pm1} \prod_i \exp\{\beta J_i S_i S_{i+1}\}$$

$$= \prod_i \sum_{S_1=\pm1} \cdots \sum_{S_N=\pm1} \exp\{\beta J_i S_i S_{i+1}\}$$

At end-point:

$$\sum_{S_N=\pm1} \exp\{\beta J_{N-1} S_{N-1} S_N\} = e^{\beta J_{N-1} S_{N-1}} + e^{-\beta J_{N-1} S_{N-1}}$$

$$= 2\cosh(\beta J_{N-1} S_{N-1})$$

Since $S_{N-1} = \pm 1$ and cosh is even, we can ignore.

Then
$$Q = \prod_{i=1}^{N-1} 2\cosh(\beta J_i)$$

$$= 2^N \prod_{i=1}^{N-1} \cosh(\beta J_i)$$

$$\langle S_i S_{i+1} \rangle = \frac{\sum S_i S_{i+1} \, e^{\beta[\sum_i J_i S_i S_{i+1}]}}{Q}$$

$$= \frac{1}{Q}\Big(\underbrace{\frac{1}{\beta}\frac{\partial}{\partial J_k} Q}_{S_i S_{i+1} Q}\Big)$$

$$= \frac{1}{\beta}\frac{\partial}{\partial J_k} \ln Q$$

$$\ln Q = N \ln 2 + \sum_{i=1}^{N-1} \ln\big(\cosh(\beta J_i)\big)$$

$$\langle S_k , S_{k+1} \rangle = \frac{1}{\cancel{\beta}\cosh(\beta J_k)} \sinh(\beta J_k)\, \cancel{\beta}$$

$$= \tanh(\beta J_k)$$

$$\langle S_k S_{k+r} \rangle = \langle S_k \underbrace{(S_{k+1} S_{k+1})}_{(\pm 1)(\pm 1)=1}(S_{k+2} S_{k+2}) \cdots (S_{k+r-1})(S_{k+r-1}) S_{k+r} \rangle$$

$$= \langle (S_k S_{k+1})(S_{k+1} S_{k+2}) \cdots (S_{k+r-1} S_{k+r}) \rangle$$

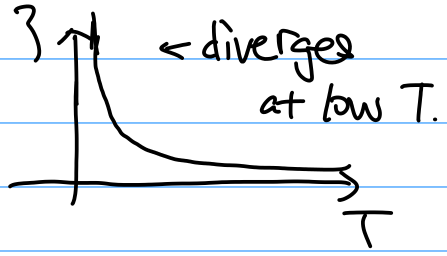
$$= \langle S_k S_{k+1} \rangle \langle S_{k+1} S_{k+2} \rangle \cdots \langle S_{k+r-1} S_{k+r} \rangle$$

$$= \langle S_k S_{k+1} \rangle^r$$

$$\boxed{\begin{gathered}\text{then } g(r) = \langle S_k S_{k+r}\rangle = \langle S_k S_{k+1}\rangle^r = \tanh(\beta J)^r \\ \text{since } g(r) \propto e^{-r/\xi} \quad \text{then } \xi = \frac{1}{\ln\left(\frac{1}{\tanh(\beta J)}\right)}\end{gathered}}$$

For $\beta J \gg 1$, $k_B T \ll J$

taylor: $\xi \to \frac{1}{2} e^{2\beta J} \gg 1$



Magnetic susceptibility:

$$\chi = \frac{\partial \langle M \rangle}{\partial H} = -\left(\frac{\partial^2 A}{\partial H^2}\right)_T = \beta\big(\underbrace{\langle M^2\rangle - \langle M\rangle^2}_{(\delta M)^2}\big)$$

$$\Rightarrow = u^2 \beta \sum_i \sum_j \langle S_i S_j \rangle - \langle S \rangle^2$$

$$\stackrel{!}{=} N u^2 \beta \underbrace{\sum g(r)}_{\approx \int d^3r\, g(r)}$$

$$g(r) \propto e^{-r/\xi}$$

at $\sim T_c$, little H gives large $\langle M \rangle$, or $\chi \sim \infty$

Mean-Field Theory for Ising Model:

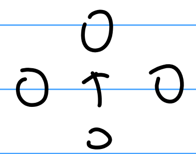
$$\mathcal{H} = -\mu H \underbrace{\sum_i S_i}_{\substack{N\langle S_i\rangle \\ Nm}} - J \sum_{\substack{ij \\ \text{pairs}}} S_i S_j$$

↳ $\mathcal{H}_{MF} = -\mu \sum_i H_i(m)\, S_i$

effective magnetic field

$$H_i = -\frac{1}{\mu}\frac{\partial \mathcal{H}}{\partial S_i}$$

$$\stackrel{!}{=} H + \frac{J}{\mu} \underbrace{\sum_{j=1}^{q} S_j}_{\text{Mean-Field: } q\langle S_i\rangle}$$



$\Rightarrow q=4$ for 2D.

Then $H_i = \langle H_i \rangle = H + \overbrace{\frac{J}{\mu} q m}^{\Delta H}$ ← Mean-Field approximation

$$m = \langle S_i \rangle = \sum_{S_i = \pm 1} \frac{1}{Q_1} e^{-\beta(-\mu H_i S_i)} S_i$$

↳ $Q_1 = \sum_{S_i=\pm 1} e^{-\beta(-\mu H_i S_i)}$

$$H_{MF} = -\mu \sum_i H_i(m) S_i$$

$$\stackrel{!}{=} -\mu\Big(H + \underbrace{\frac{J}{\mu} q m}_{\Delta H.}\Big) \sum_i S_i$$

$$\stackrel{!}{=} -\mu (H + \Delta H) \sum_i S_i$$

Self-consistent Eq: $m = \langle S_i \rangle = \tanh(\beta\mu H + \beta J q m)$

For $H=0$, is $m(H=0,T) \neq 0$?

↳ $m = \tanh(\beta J q m)$, with critical point $q\beta J = 1$
$T_c = q\frac{J}{k_B}$

Phase transition when $q\beta J > 1$.

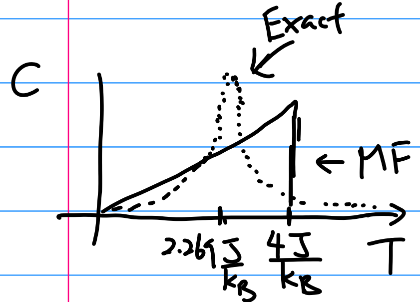
Dimension	T_c exact (Ising)	MFT
1	0	$2\ J/k_B$
2	$2.269\ J/k_B$	$4\ J/k_B$
3	$4.513\ J/k_B$	$6\ J/k_B$

In Mean-Field Theory:

$$\frac{A}{N} = \frac{k_BT}{2}\ln\left(\frac{1-m^2}{4}\right) + \frac{m^2Jq}{2}$$

as $T > T_c$: $\frac{A}{N} = \frac{k_BT}{2}\ln\left(\frac{1}{4}\right) = -k_BT\ln(2)$

2D



$S = Nk_B\ln(2) \Rightarrow C = 0$ ← which is wrong.

Perturbation Theory:

$$\mathcal{H}^{(0)} \rightarrow \mathcal{H}^{(0)} + \Delta\mathcal{H}$$

$$E_\nu^{(0)} \rightarrow E_\nu^{(0)} + \Delta E_\nu$$

$$Q = \sum_\nu e^{-\beta(E_\nu^{(0)} + \Delta E_\nu)}$$

$$\overset{!}{=} \sum_\nu e^{-\beta\Delta E_\nu} e^{-\beta E_\nu^{(0)}}$$

$$\overset{!}{=} Q^{(0)} \sum_\nu \frac{e^{-\beta E_\nu}}{Q^{(0)}} e^{-\beta\Delta E_\nu}$$

$$\overset{!}{=} Q^{(0)} \langle e^{-\beta\Delta E_\nu} \rangle_0$$

Taylor Expand: $\langle e^{-\beta\Delta E_\nu} \rangle$

$$\langle e^{-\beta\Delta E_\nu} \rangle = \langle 1 - \beta\Delta E_\nu + \cdots \rangle$$

$$\approx 1 - \beta\langle \Delta E_\nu \rangle$$

$$\approx e^{-\beta\langle \Delta E_\nu \rangle_0}$$

$$Q \cong Q^{(0)} e^{-\beta\langle \Delta E_\nu \rangle_0} = Q^{(0)} e^{-\beta\langle E - E_\nu^{(0)} \rangle}$$

Upper bound: $\langle e^{-\beta\Delta E} \rangle_0 = e^{-\beta\langle \Delta E_0 \rangle} \langle e^{-\beta(\Delta E - \langle \Delta E \rangle_0)} \rangle$

$$\hookrightarrow \geq e^{-\beta\langle \Delta E \rangle_0} \langle \underbrace{1 - \beta(\Delta E - \langle \Delta E \rangle_0)}_{1 - \beta(\cancel{\langle \Delta E \rangle_0} - \langle E \rangle)} \rangle_0 .$$

$$\langle e^{-\beta\Delta E} \rangle_0 \geq e^{-\beta\langle \Delta E \rangle_0}$$

or $\quad Q \geq Q^{(0)} e^{-\beta\langle\Delta E\rangle_0}$

or $\quad -k_BT\ln Q \leq -k_BT\ln Q^{(0)} + \langle\Delta E\rangle_0$

$$\boxed{A \leq -k_BT\ln Q^{(0)} + \langle\Delta E\rangle_0}$$ Gibbs-Bogoliubov -Feynman bound.

To mean-field theory: $\quad H_{MF} = -\mu(H+\Delta H)\sum_{S_i}^{N} S_i$

$$A_{MF} = -k_BT\ln Q_{MF}$$
$$\stackrel{!}{=} -Nk_BT\ln\left(2\cosh\left[\beta\mu(H+\Delta H)\right]\right)$$
$$m = \tanh\left(\beta\mu(H+\Delta H)\right)$$

Now check whether Mean-Field theory give best approximation.

$$H = H_{MF} + \Delta H$$

$$\Delta H = \left(-J\sum_{ij} S_iS_j + \mu\Delta H\sum_i S_i\right)$$
$$H^{exact}_{Interaction} - H^{MF}_{Interaction}$$

$$\langle\Delta H\rangle = \langle\Delta E\rangle_0 = -\frac{1}{2}JNqm^2 + \mu\Delta HNm$$

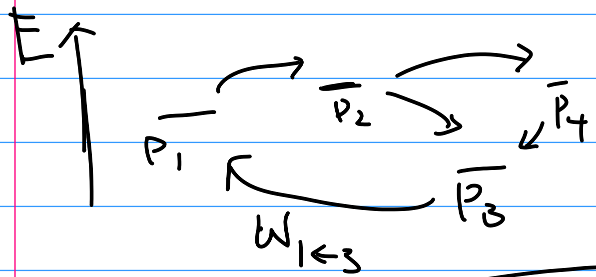
$$A \le A_{MF} + \langle \Delta E \rangle_0 = -Nk_BT \ln\left[2\cosh\left(\beta\mu(H+\Delta H)\right)\right]$$
$$-\frac{1}{2}JNq\,m^2 + \mu\Delta H N m$$

Get Minimum: $\partial\left(A_{MF} + \langle \Delta E\rangle_{MF}\right) = 0$

$$\frac{\partial}{\partial \Delta H}\left(A_{MF} + \langle\Delta E\rangle_{MF}\right) = -\cancel{N\mu m} - JqNm\frac{\partial m}{\partial \Delta H} + \cancel{\mu N m}$$
$$+\mu\Delta H N\frac{\partial m}{\partial \Delta H}$$
$$\stackrel{!}{=} 0$$

then $\Delta H = \dfrac{Jqm}{\mu}$ ← Same as mean-field theory.

Monte-Carlo



Masters Equation.

rate going from $P_j \rightarrow P_i$

$$\frac{dP_i}{dt} = \sum_{j \neq i} \left(W_{i\leftarrow j} P_j - W_{j \leftarrow i} P_i \right)$$

$$\frac{dP_i}{dt} = \sum_{j \neq i} \left(w_{ij} P_j - W_{ji} P_i \right)$$

Thermo equilibrium $\Rightarrow \dfrac{dP_i}{dt} = 0$

$$\frac{dP_i}{dt} = 0 = W_{ij} P_j - W_{ji} P_i = 0$$

Detailed Balance.

$$\boxed{\frac{W_{i\leftarrow j}}{W_{j\leftarrow i}} = \frac{P_i}{P_j} = e^{-\beta(E_i - E_j)}}$$

Classical Fluids:

For classical: $\rho \lambda_{th}^3 \ll 1$, or μ large negative.

For Mercury (liquid at room temperature):

$$\left.\begin{array}{l} \rho_M = 13.5 \text{ g/cm}^3 \\ \bar{m} = 200.6 \text{ amu} \end{array}\right\} \quad \rho = \frac{N}{V} = \frac{\rho_m}{\bar{m}} = 4\times10^{22} \text{ cm}^{-3}$$

$$\lambda_{th} = 1\times10^{-10} \text{ cm}$$

$$\text{So } \rho\lambda_{th}^3 \sim 10^{-5}$$

So we can do classical:

$$\mathcal{H}(\vec{r}_1, \vec{r}_2, \vec{r}_3 \cdots \vec{r}_N, \vec{p}_1 \cdots, \vec{p}_N) = \mathcal{H}(r^N, p^N)$$

$$Q = \sum_\nu e^{-\beta E_\nu} = \frac{1}{(2\pi\hbar)^{3N} N!} \int dr^N \int dp^N \, e^{-\beta H(r^N, p^N)}$$

$$H(r^N, p^N) = \underbrace{K(p^N)}_{\sum_i \frac{p_i^2}{2m}} + U(r^N)$$

$$Q = \underbrace{\frac{1}{N! (2\pi\hbar)^{3N}} \int dp^N \exp\left[-\beta \sum_i \frac{p_i^2}{2m}\right]}_{\frac{1}{V^N}\frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N = \frac{1}{V^N} Q_{\text{ideal gas}}} \int dr^N \, e^{-\beta U(r^N)}$$

$$\boxed{Q = \underbrace{\frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N}_{Q\ \text{ideal}} \underbrace{\frac{1}{V^N}\int dr^N e^{-\beta U(r^N)}}_{Q\ \text{config}}}$$

$$n(\vec{p}) = \frac{N\int d^3p_2 \cdots \int d^3p^N \int dr^N e^{-\beta H}}{\int dp^N \int dr^N e^{-\beta H}}.$$

$$= \frac{N\int d^3p_2 \cdots \int d^3p_N \, e^{-\beta \sum p_i^2/2m}}{\int dp^3_N \, e^{-\beta \sum p_i^2/2m}}$$

remove position dependent since integrate all position, so once we divide, they cancel

$$n(\vec{p}) = \frac{N}{(2\pi m k_B T)^{3/2}} e^{-\beta \frac{|\vec{p}|^2}{2m}}$$

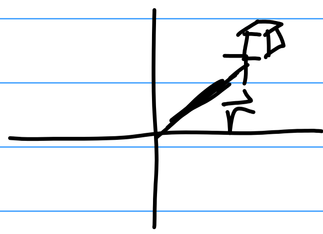
← reduced distribution for momentum is the same as ideal gas.

position reduced distribution.

N-choice.

$$\rho(\vec{r}) = \frac{N\int d^3r_2 \cdots\cdots \int d^3r_N \, e^{-\beta U(r^N)}}{\int d\vec{r}_1^3 \cdots \int d^3r_N \, e^{-\beta U(r^N)}}$$

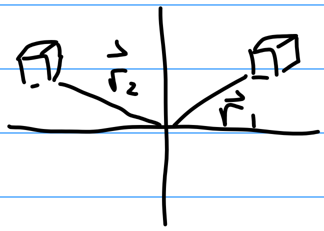
$$\overset{!}{=} \frac{N}{V} = \rho$$



$\rho(r)d^3r = \#$ in box

$$\rho^{(2/N)}(\vec{r}_1,\vec{r}_2) = \frac{N(N-1)\int d^3r_3 \cdots \int d^3r_N\, e^{-\beta U(r^N)}}{\int d^3r_1 \cdots \int d^3r_N\, e^{-\beta U(r^N)}}$$

If $U=0$, then $\rho(\vec{r}_1,\vec{r}_2) = \frac{N(N-1)}{V^2} = \rho^2$



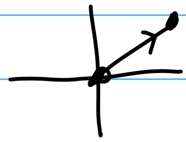
$d^3r_1\, d^3r_2\, \rho(\vec{r}_1,\vec{r}_2) \equiv$ Joint # of particles in box.

$$g(\vec{r}_1,\vec{r}_2) = \frac{\rho^{(2/N)}(\vec{r}_1,\vec{r}_2)}{\rho^2}$$ $\Leftarrow$ pair correlation function.

Should related to the distance between.

$g(\vec{r}_1,\vec{r}_2) \longrightarrow g(|\vec{r}_1,\vec{r}_2|) = g(r)$: radial distribution func.

then $\rho g(r)$: density of particles at r given a particle at $r=0$, $g(0,\vec{r})$



Pair potential: $U(\vec{r}_1,\vec{r}_2 \cdots \vec{r}_N) \approx \sum_{(ij)} U(|\vec{r}_i - \vec{r}_j|) = U(r)$

$$\begin{cases} \langle U(r^N)\rangle = \frac{1}{2} V\rho^2 \int_0^\infty 4\pi r^2 dr\, g(r)\, U(r) \\ \frac{\langle E\rangle}{N} = \frac{3}{2}k_BT + \frac{1}{2}\rho \int_0^\infty 4\pi r^2 dr\, g(r)\, U(r) \\ P = \rho k_BT\left(1 - \frac{\rho}{6k_BT}\int_0^\infty 4\pi r^2 dr\, g(r)\, r\frac{dU}{dr}\right) \end{cases}$$