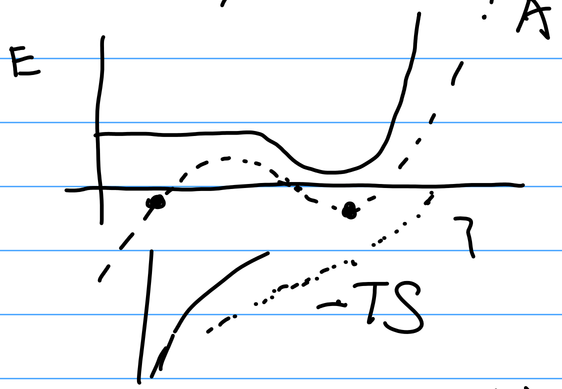
Minimize Free energy:

$$A = E - TS$$

consider an order parameter, ξ

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

An example of $E(\xi)$:



two ξ 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:

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

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

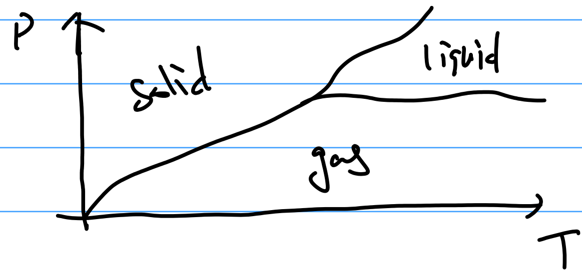
$$\boxed{E_{MF} = -N\rho a}$$

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

For van-der-Waals gas

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

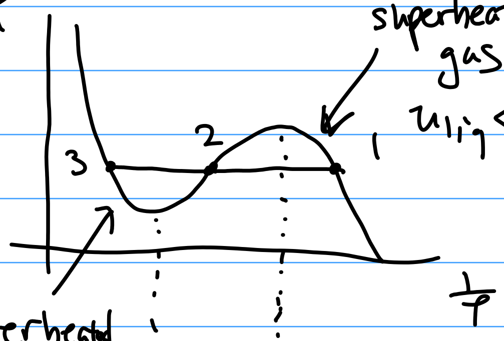
This phase transition has a latent heat:



Heating but stays at constant temp.

To find the latent heat:

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



superheated gas

$u_{liq} < u_{gas}$

Superheated liquid

$u_{liq} > u_{gas}$

metastable

unstable, So it goes through line rather than curve.

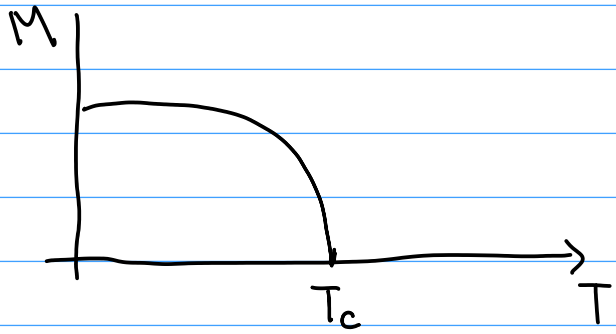
$$\int_1^3 dG = 0$$

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

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

Continuous Phase Transition: No latent heat.

1st order Phase Transition: Has Latent heat



$$\partial A = -SdT - mdH$$

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

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

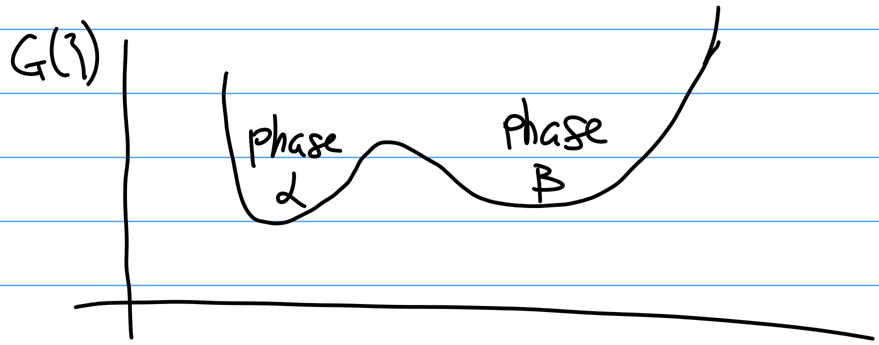
$$\frac{\partial M}{\partial H} = \chi \propto \frac{1}{\left(1-\frac{T}{T_c}\right)^{\gamma}} = \frac{1}{\tau^{\gamma}} \qquad \gamma \cong 1.3$$

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

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

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

Landau Theory:



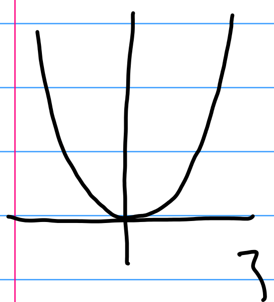
Near critical point:

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

depend on T

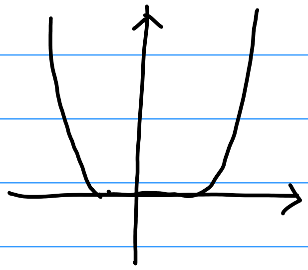
$T > T_c$

$G_2, G_4 > 0$



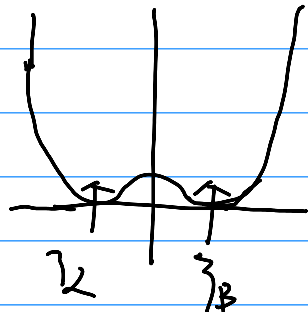
$T = T_c$

$G_2 = 0$



$T < T_c$

$G_2 < 0, \quad G_4 > 0$



symmetry breaking

External Field: $G \rightarrow G - uH\langle m \rangle$

applied field

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

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

$\simeq uH$

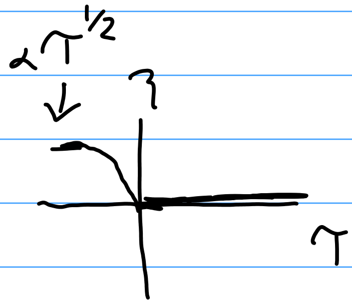
magnetic field

kinetic

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

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

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



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

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

Since $\eta \propto \tau^{\beta}$ $\boxed{\text{Find } \beta = \frac{1}{2}}$

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

ignore higher order.

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

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

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

Ising Model:

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

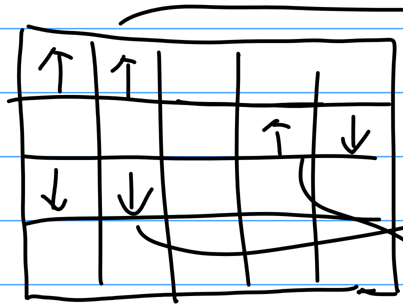
⇒ Each lattice can only be in one of two states. ↑↓

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

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

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

J = Interaction strength
H = external field
μ = Magnetic moment



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

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

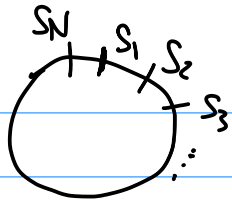
} lower energy

$-J(-1)(1) = +J$ → Higher Energy

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

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

Consider 1D model:



$$Q = \sum_{S_1=\pm 1} \cdots \sum_{S_N=\pm 1} \exp\left[\underbrace{K S_i S_{i+1} + \tfrac{1}{2} h (S_i + S_{i+1})}_{\text{4 possibilities in the end.}}\right]$$

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

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

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

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

Transfer Matrix:

$$\begin{array}{cc} (1,1) & (-1,1) \end{array}$$

$$P_{i,j} = \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix}$$

$$\begin{array}{cc} (-1,1) & (-1,-1) \end{array}$$

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

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

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

$$Q \approx \lambda_1^{\,N}$$

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

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

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

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

$$Q = (2\cosh(K))^N$$
$$A = -Nk_BT\ln(2\cosh(K))$$

$$\langle M\rangle = -\left(\frac{\partial A}{\partial H}\right)_T \qquad dE = TdS - MdH$$
$$dA = -SdT - MdH$$

then

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

Spontaneous Magnetization

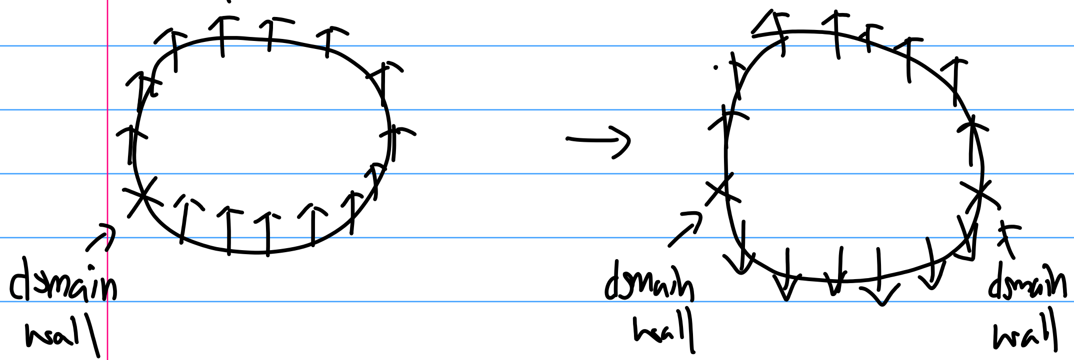
<u>$M(H=0,T)$</u>

as $\lim_{h\to 0} \frac{N\mu\sinh(h)}{e^{-2K}} \to 0$ 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?:



$\Delta E = 2J + 2J$

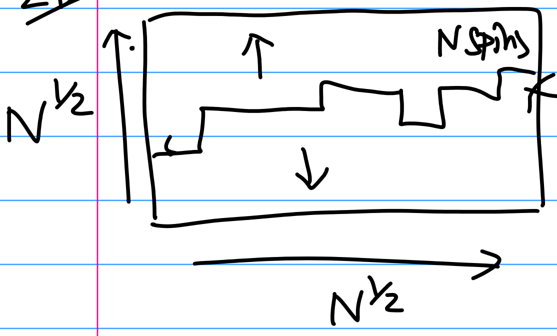
choice of putting wall

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

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

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.

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

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

$$\simeq \underbrace{2JL - k_B T L \ln(3)}_{N^{1/2}} - \frac{1}{2} k_B T \ln(N) - k_B T \ln 2$$

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:

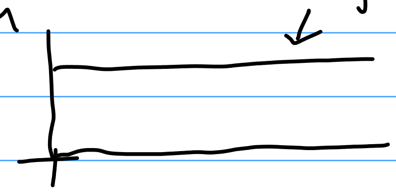
$$Q = \left[2\cosh(\beta J) e^{I}\right]^N$$

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

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

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

Correlation Function:



ensemble average

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

ξ ← 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:

$\underline{H=0}$:

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

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

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

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

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

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

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

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

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

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

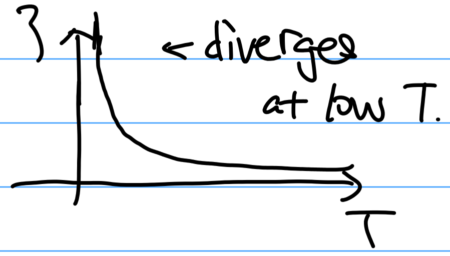
$$= \langle S_k S_{k+1}\rangle\langle S_{k+1} S_{k+2}\rangle\cdots\cdots\langle S_{k+r-1} S_{k+r}\rangle$$

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

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

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

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



Magnetic susceptibility:

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

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

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

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

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

Mean-Field Theory for Ising Model:

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

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

↑ effective magnetic field

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

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

$\Rightarrow q = 4$ for 2D.

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

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

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

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

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

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

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

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

$\hookrightarrow m = \tanh(\beta J q m)$, with critical point $q\beta J = 1$

$T_c = q \frac{J}{k_B}$

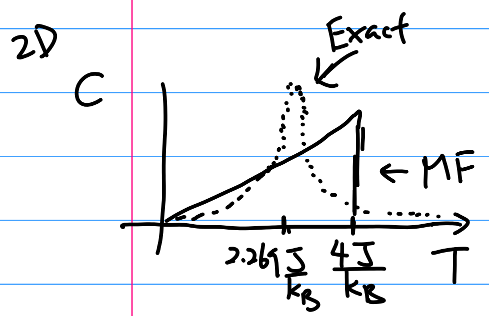
Phase transition when $q\beta J > 1$.

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:

$$\frac{A}{N} = \frac{k_B T}{2} \ln\left(\frac{1-m^2}{4}\right) + \frac{m^2 J q}{2}$$

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



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

Perturbation Theory:

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

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

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

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

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

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

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

$$A_{MF} = -k_BT \ln Q_{MF}$$

$$\stackrel{!}{=} -Nk_BT \ln \left(2\cosh[\beta\mu(H+\Delta H)]\right)$$

$$m = \tanh(\beta\mu(H+\Delta H))$$

Now check whether Mean-Field theory give best approximation.

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

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

$$H^{exact}_{Interaction} - H^{MF}_{Interaction}$$

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

$$A \le A_{MF} + \langle \Delta E \rangle_0 = -Nk_B T \ln[2\cosh(\beta\mu(H+\Delta H))]$$

$$- \frac{1}{2} J N q m^2 + \mu \Delta H N m$$

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

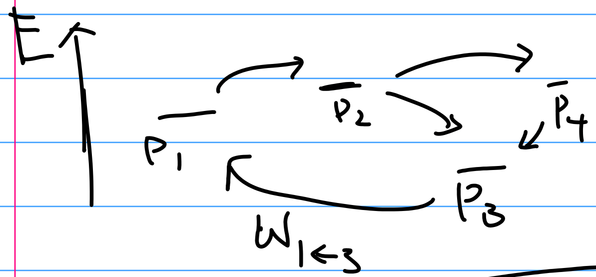
$$\frac{\partial}{\partial \Delta H}\left(A_{MF} + \langle \Delta E \rangle_{MF}\right) = -\cancel{N\mu m} - J q N m \frac{\partial m}{\partial \Delta H} + \cancel{\mu N m}$$

$$+ \mu \Delta H N \frac{\partial m}{\partial \Delta H}$$

$$\stackrel{!}{=} 0$$

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

Monte-Carlo



Masters Equation.

rate going from $P_j \to P_i$

$$\boxed{\begin{aligned} \frac{dP_i}{dt} &= \sum_{j\neq i} \left(W_{i\leftarrow j} P_j - W_{j\leftarrow i} P_i \right) \\ \frac{dP_i}{dt} &= \sum_{j\neq i} \left(W_{ij} P_j - W_{ji} P_i \right) \end{aligned}}$$

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):

$$\left.\begin{aligned} \rho_M &= 13.5\ g/cm^3 \\ \bar{m} &= 200.6\ amu \end{aligned}\right\} \quad \rho = \frac{N}{V} = \frac{\rho_m}{\bar{m}} = 4\times 10^{22}\ cm^{-3}$$

$$\lambda_{th} = 7\times 10^{-10}\ cm$$

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

So we can do classical:

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

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

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

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

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

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

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

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

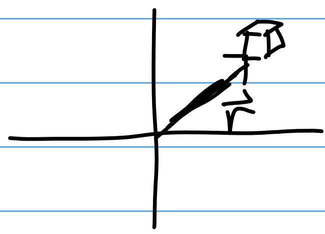
$$n(\vec{p}) = \frac{N}{(2\pi m k_B T)^{3/2}} e^{-\beta \frac{|\vec{p}|^2}{2m}}$$

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

position reduced distribution.

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

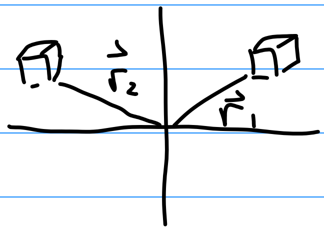
$$= \frac{N}{V} = \rho$$



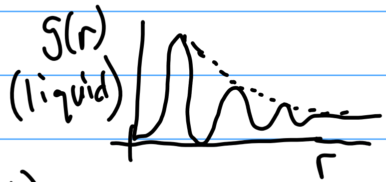
$\rho(r) d^3r = \#$ in box

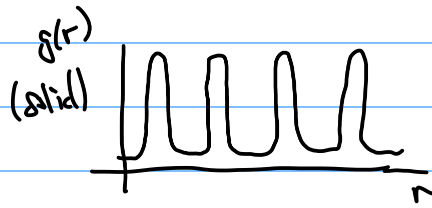
$$\Rightarrow \rho^{(2/N)}(\vec{r}_1,\vec{r}_2) = \frac{N(N-1)\int d^3r_3 \cdots \int d^3r_N\, e^{-\beta U(r^N)}}{\int d^3r_1 \cdots \int d^3r_N\, e^{-\beta U(r^N)}}$$

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) = $ Joint # of particles in box.



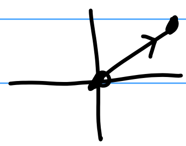


$$g(\vec{r}_1,\vec{r}_2) = \frac{\rho^{(2/N)}(\vec{r}_1,\vec{r}_2)}{\rho^2}$$ $\Leftarrow$ pair correlation function.

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.

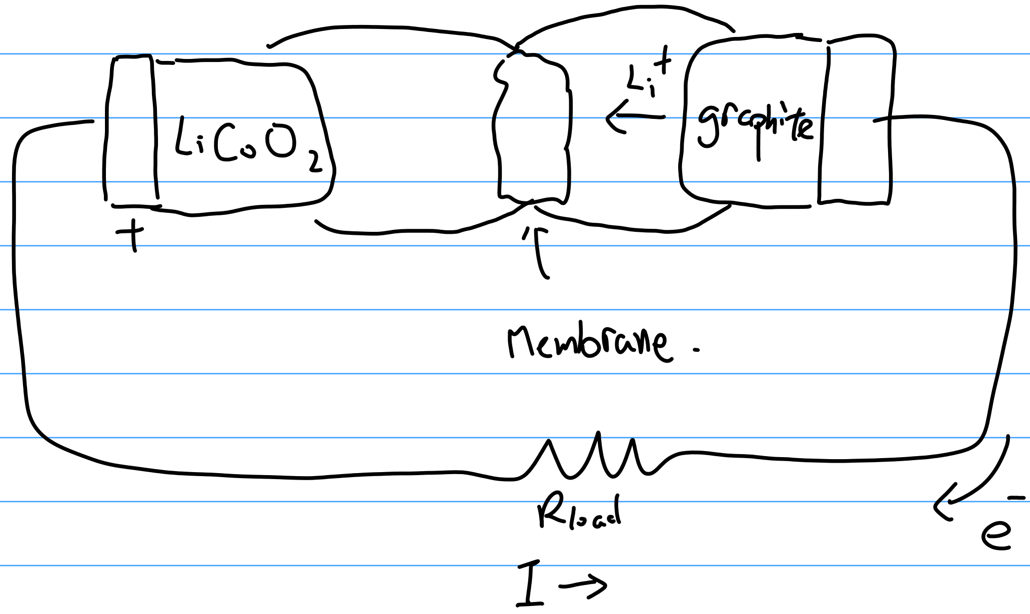
then $\rho g(r)$: density of particles at r given a particle at $r=0$, $g(0,\vec{r})$



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

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

Nonequilibrium Stat Mechanic:



Ions driven by gradient in μ/T
e^- driven by voltage current:

$$\vec{J}(t \mid \lambda F) = \lambda \vec{J}(t \mid F) \quad \text{Linear Response.}$$

force.

$$\vec{J}_{mass} \propto -\vec{\nabla}(\mu/T)$$

$$\vec{J}_{charge} \propto -\vec{\nabla}\phi$$

Initial conditions

Assume Observable: $A(t) = A(t \mid r^N p^N)$

$$\langle A \rangle = \langle A(t) \rangle = \int dr^N \int dp^N \, f(r^N, p^N) \, A(t \mid r^N p^N)$$

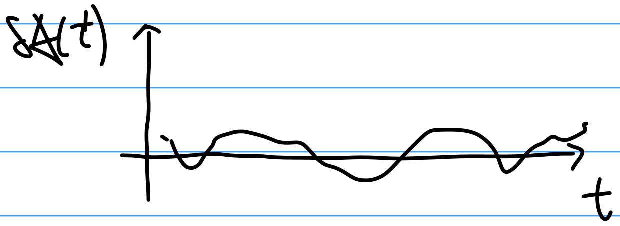
$$f(r^N, p^N) \propto e^{-\beta H(r^N, p^N)}$$

equilibrium distribution.

If want dynamics, need non-equilibrium.

$$f \rightarrow F(r^N, p^N)$$ = non-equilibrium distribution.
(Initial Condition distribution)

$$\bar{A}(t) = \int dr^N \int dp^N \; F(r^N, p^N) \, A(t \mid r^N, p^N)$$



$$\delta A(t) = A(t) - \langle A \rangle$$ ← Not square-integrable, since goes on forever

$$\langle \delta A(t) \rangle = \langle A \rangle - \langle A \rangle = 0$$

Define: $k(t) = \langle \delta A(0) \, \delta A(t) \rangle = \langle A(0) A(t) \rangle - \langle A \rangle^2$

at equilibrium should depend upon separation between times

$$k(t) = \langle \delta A(t') \, \delta A(t'') \rangle = \langle A(t') A(t'') \rangle - \langle A \rangle^2$$

$$k(t) = \int dr^N \int dp^N \, f(r^N, p^N) \, \delta A(t') \, \delta A(t'')$$ for classical system

$$k(t) = \langle \delta A(0) \, \delta A(t) \rangle = \langle \delta A(-t) \, \delta A(0) \rangle = k(-t)$$

at large times, $\delta A(t)$ should be uncorrelated with $\delta A(0)$

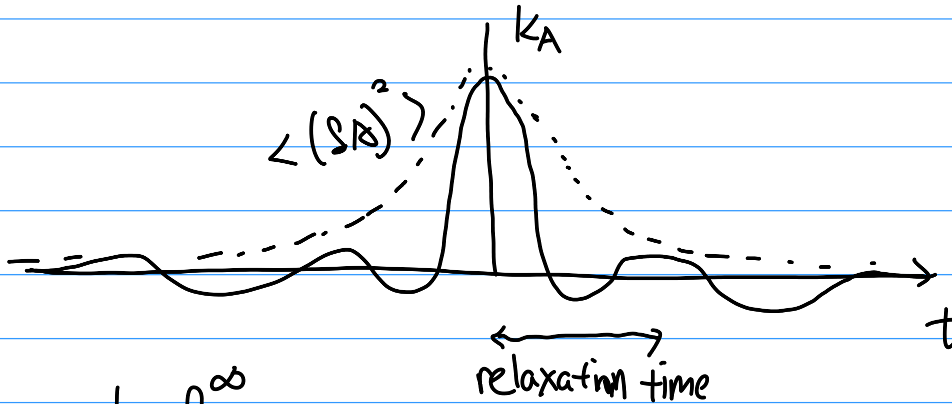
$$\lim_{t \to \infty} k(t) = 0$$

In QM:

$$\underbrace{\delta\hat{A}(t)}_{\text{Heisenberg}} = \underbrace{e^{i\hat{H}t/\hbar}\,\delta\hat{A}\,e^{-i\hat{H}t/\hbar}}_{\text{Schrodinger}}$$

In general: $[\delta A(t'), \delta A(t'')] \neq 0$

$$K(t)_{QM} = \frac{1}{2}\langle \delta\hat{A}(t')\,\delta\hat{A}(t'') + \delta\hat{A}(t'')\,\delta\hat{A}(t')\rangle$$



$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} F(\omega)$$

$$F(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} f(t)$$

$$\delta A(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\,\delta A(t) \quad \Rightarrow \quad \langle \delta A(\omega)\rangle = 0$$

Power: $$P = \lim_{T\to\infty}\frac{1}{T}\int_{-T/2}^{T/2} dt\,\langle(\delta A(t))^2\rangle$$

$$P = \int_{-\infty}^{\infty} d\nu\, S_A(\nu) \qquad \text{where} \quad \underset{\substack{\uparrow \\ \text{cycles per s}}}{\nu} = \frac{\omega^{\to \text{rad/s}}}{2\pi}$$

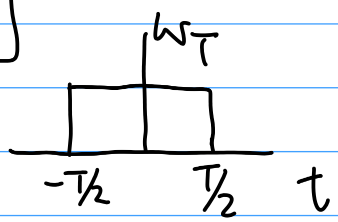
$$= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\underset{\substack{\uparrow \\ \text{power spectrum density}}}{S_A(\omega)}$$

Theorems of Fourier Transform:

① Parseval's Theorem: $$\int_{-\infty}^{\infty} dt\, |f(t)|^2 = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} |F(\omega)|^2$$

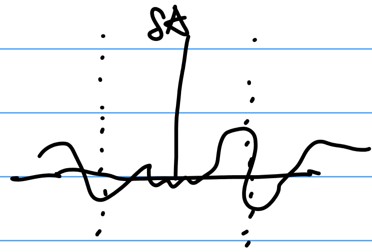
② If $h(t) = f(t) \otimes g(t) = \int_{-\infty}^{\infty} dt\, g(\tau - t) f(t)$

then $H(\omega) = F(\omega) G(\omega)$

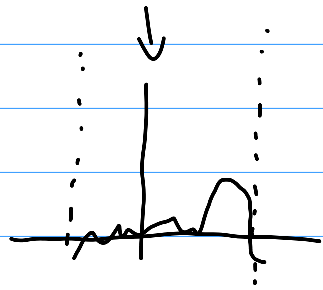


$\Rightarrow \quad \delta A^{(T)} = \delta A(t)\, \underset{\uparrow}{W_T(t)}$

windows function



then $\quad \delta A^{(T)}(t) \rightarrow \delta A^{(T)}(\omega)$



with theorem 1 $$\int_{-\infty}^{\infty} dt\, |\delta A^{(T)}(t)|^2 = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} |\delta A^{(T)}(\omega)|^2$$

$$\underbrace{\lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{\infty} dt\, |\delta A^{(T)}(t)|^2}_{P} = \lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} |\delta A^{(T)}(\omega)|^2$$

, then $S_A = \lim_{T\to\infty} |\delta A^{(T)}(\omega)|^2$

$$S_A = \frac{1}{T} \lim_{T\to\infty} \left[(\delta A^{(T)}(\omega))^* \delta A^{(T)}(\omega) \right]$$

Since $\quad (\delta A(\omega))^* = FT\{\delta A(-t)\} = \int \frac{d\omega}{2\pi} e^{-i\omega t} \delta A(-t)$

with theorem 2

$$(\delta A^{(T)}(\omega))^* (\delta A^{(T)}(\omega)) = FT\{\delta A^{(T)}(-t)\} FT\{\delta A^{(T)}(t)\}$$

↑ It is convolution in t-space suggested by theorem 2

Then $\quad |\delta A^{(T)}(\omega)|^2 = \int d\tau\, e^{i\omega\tau} \int dt\, \delta A^{(T)}(t-\tau)\, \delta A^{(T)}(t)$

$$S_A(\omega) = \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \underbrace{\lim_{T\to\infty} \frac{1}{T} \int_{-\infty}^{\infty} dt\, \delta A(t-\tau)\, \delta A(t)}_{\text{due to ergodic principle}}$$

$\langle \quad \rangle = \lim_{T\to\infty} \int$

ensemble average = time average.

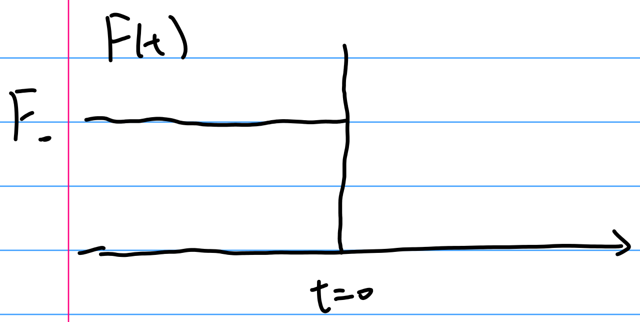
Wiener-Khinchin Theorem

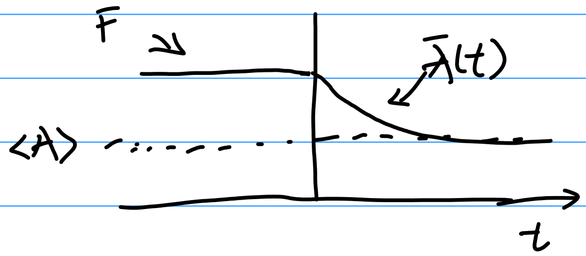
$$\boxed{S_A(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \underbrace{\langle \delta A(0)\, \delta A(t) \rangle}_{K_A(t)} = 2\int_0^{\infty} dt\, \cos\omega t\, \langle \delta A(0)\, \delta A(t) \rangle}$$

S_A: Two-sided power spectral density of fluctuations, δA

and

$$\boxed{\langle \delta A(0)\, \delta A(t) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} S_A(\omega) \stackrel{!}{=} 2\int_0^{\infty} d\nu\, S_A(\nu) \cos(2\pi\nu t)}$$





Onsager Regression Postulate

$$\frac{\bar{A}(t)}{\bar{A}(0)} = \frac{K_A(t)}{K_A(0)}$$

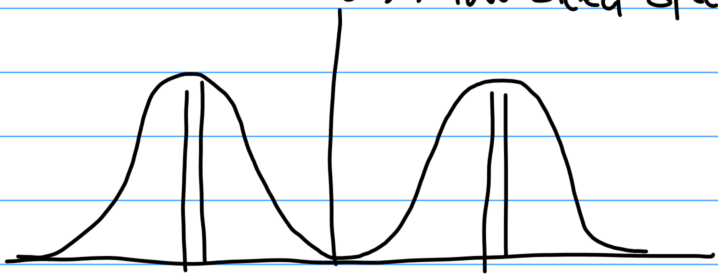
Given $K_A(t)$: even function.

then $S_A^*(w) = S_A(w) = \text{Real}.$

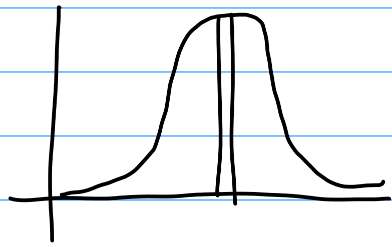
If $K_A(t) = \text{Real}$, then $S_A(-w) = S_A^*(w)$

$$\left.\begin{aligned} S_A(-w) &= S_A(w) \\ S_A(w) &= S_A^*(w) \end{aligned}\right\} S_A(w) = \text{even and real.}$$

$S(\omega)$, two sided spectral density.



$W_A(\omega)$



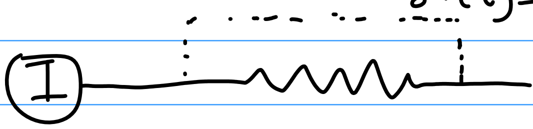
$= 2S_A(\omega)$ for $\omega \neq 0$

$= S_A(\omega=0)$ for $\omega = 0$.

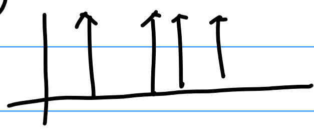
$\boxed{\begin{aligned} &W_A(\omega): \text{ single-sided.} \\ &W_A(\nu) = 2\int_{-\infty}^{\infty} dt\, e^{i(2\pi\nu t)} \langle \delta A(0)\, \delta A(t)\rangle = 4\int_0^{\infty} dt \cos(2\pi\nu t)\, k_A(t) \\ &\text{where} \quad k_A(t) = \langle \delta A(0)\, \delta A(t)\rangle = \int_0^{\infty} d\nu \cos(2\pi\nu t)\, W_A(\nu) \end{aligned}}$

Ex:

$\delta V(t) = R\,\delta I(t)$



$I(t)$



t

$I(t) = \sum_i e\,\delta(t - t_i)$

$k_I(t) = \langle \delta I(t')\, \delta I(t'')\rangle$

$\overset{!}{=} \langle I(t')\, I(t'')\rangle - \langle I\rangle^2$

$t'' - t' = t$

$\overset{!}{=} \lim_{T\to\infty} \frac{1}{T}\int_{-T/2}^{T/2} dt'\, I(t')\, I(t'+t) - \langle I\rangle^2$

$$K_I(t) = \lim_{T\to\infty} \frac{e^2}{T}\int_{-T/2}^{T/2} dt' \left(\sum_i e\,\delta(t'-t_i)\right)\left(\sum_j e\,\delta(t'+t-t_j)\right)$$

$$= \lim_{T\to\infty} \frac{e^2}{T}\int_{-T/2}^{T/2} dt' \sum_i \sum_j \delta(t-t_i)\,\delta(t'-(t_j-t))$$

<u>lim $t \to 0$:</u>

$$K_I(0) = \lim_{T\to\infty} \frac{e^2}{T}\int_{-T/2}^{T/2} dt' \sum_i \delta(t-t') = \frac{\overset{\#\text{ of } e^-}{N} e^2}{T}$$

then $K_I(t) = K_I(0)\,\delta(t) = \frac{Ne^2}{T}\delta(t) = \bar{I} e\,\delta(t)$

then $W_I(\nu) = 2\int_{-\infty}^{\infty} dt\, e^{i2\pi\nu t}\, e\bar{I}\,\delta(t)$

$W_I(\nu) = 2e\bar{I}$ ← shot noise. (constant)

Detector with bandwidth: $\Delta\nu$

$$\langle(\delta I)^2\rangle = \int_0^{\Delta\nu} d\nu\, W_I(\nu) = 2e\bar{I}\,\Delta\nu$$

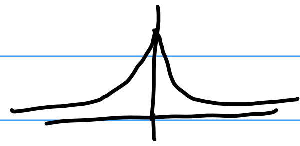
$\sqrt{\langle(\delta I)^2\rangle} = \sqrt{2e\bar{I}\Delta\nu}$ = Shot Noise

since $\bar{I} \propto N$

$\sqrt{\langle(\delta I)^2\rangle} \propto \sqrt{N}$ → Poisson Statistics.

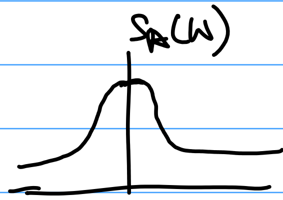
Second example:

if: $\langle \delta A(0)\, \delta A(t) \rangle = \langle (\delta A)^2 \rangle e^{-t/\tau}$



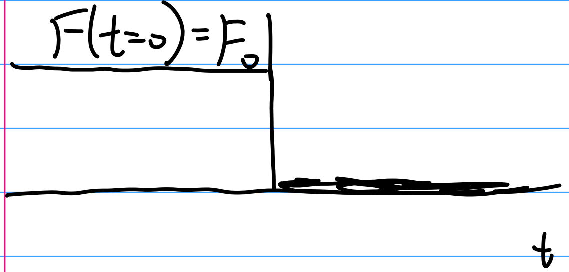
$$\frac{1}{\langle (\delta A)^2 \rangle} S_A = \int_{-\infty}^{\infty} dt \; e^{i\omega t} \; e^{-|t|/\tau}$$

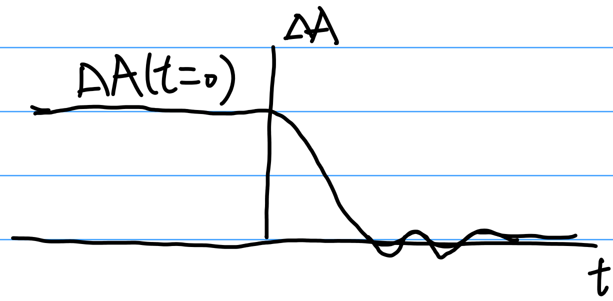
$$S_A(\omega) = \langle (\delta A)^2 \rangle \frac{2\tau}{1+\omega^2\tau^2} \xrightarrow{\text{Lorentzian}}$$



Fluctuation is related to Response of a drive:

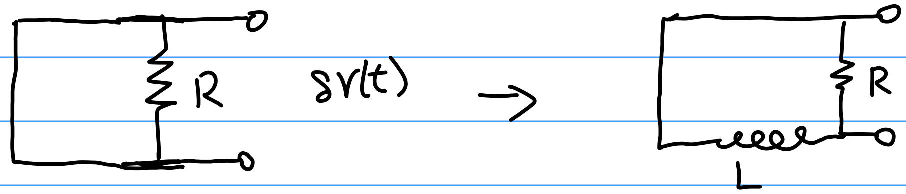
Onsager Regression Hypothesis:





$$\frac{\Delta \bar{A}(t)}{\Delta \bar{A}(0)} = \frac{K_A(t)}{K_A(0)}$$

ex: Johnson Noise:



Kirchoff's law: $IR + L\frac{\partial I}{\partial t} = 0$

$$\frac{dI}{\partial t} = -\frac{R}{L} I \Rightarrow I(t) = I_0 e^{-t/\tau} \qquad \tau = L/R$$

then $$k_I(t) = \frac{\Delta \bar{I}(t)}{\Delta \bar{I}(0)} k_I(0)$$

$$k_I(t) \overset{!}{=} \frac{I(t)}{I(0)} k_I(0) = \langle(\delta I)^2\rangle e^{-t/\tau}$$

$$W_I(\nu) = 2S_I(\nu) = 2\int_{-\infty}^{\infty} dt\, e^{i\omega t} k_I(t)$$
$$\overset{!}{=} 4\tau \langle(\delta I)^2\rangle \frac{1}{1+\omega^2\tau^2}$$

In classical limit, $\mathcal{H} = \frac{1}{2} L I^2 = \frac{1}{2} L \langle(\delta I)^2\rangle$

then $\langle E\rangle = \frac{1}{2} k_B T$

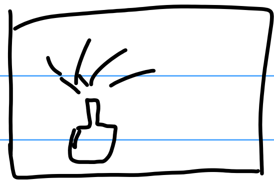
then $$\frac{1}{2} k_B T = \frac{1}{2} L \langle(\delta I)^2\rangle$$
↳ $$\langle(\delta I)^2\rangle = \frac{k_B T}{L}$$

$$W_I(\omega) = 4\left(\frac{\cancel{L}}{R}\right)\left(\frac{k_B T}{\cancel{L}}\right)\frac{1}{1+\omega^2\tau^2} \cong \frac{4k_B T}{R} \quad \text{for } \omega \ll \frac{1}{\tau}$$

since $\delta V = R\,\delta I \Rightarrow (\delta V)^2 = R^2 (\delta I)^2 \Rightarrow W_V = R^2 W_I$

↳ $$\boxed{W_V(\nu) = 4R\, k_B T}$$

Third Example: Diffusion:



let $\bar{\rho}(r,t) = n(r,t)$

flow per area

$$\frac{\partial}{\partial t}\int_V d^3\vec{r}\, n(\vec{r},t) = -\int_{\text{surface}} \partial\vec{\sigma}\cdot\vec{J}(\vec{r},t)$$

$$= -\int_V d^3r\, \vec{\nabla}\cdot\vec{J}(\vec{r},t)$$

then $\boxed{\text{Continuity:}\quad \frac{d}{dt} n(\vec{r},t) = -\vec{\nabla}\cdot\vec{J}(\vec{r},t)}$

expect $\vec{J} \propto -\vec{\nabla}\left(\frac{\mu}{T}\right)$

and $\Delta\mu \propto \Delta n$

So $\vec{J} \propto -\vec{\nabla} n$

$\boxed{\text{Fick's Law:}\quad \vec{J} = -D\vec{\nabla} n}$

All together: $\frac{\partial n}{\partial t} = -\vec{\nabla}\cdot(-D\vec{\nabla} n)$

Diffusion Eq: $\boxed{\frac{\partial n}{\partial t} = D\nabla^2 n}$

$$n(r, t=0) = \delta^3(\vec{r} - \vec{r}_0)$$

$$g(\vec{r}, t | \vec{r}_0) = \frac{1}{(4\pi D t)^{3/2}} e^{-|\vec{r}-\vec{r}_0|^2/4Dt}$$

green's function

$$(\delta r)^2 \propto 4Dt$$

$$\vec{r}^{\,2}(t) = \int d^3\vec{r}\; r^2 g(\vec{r}, t)$$

$$\overset{!}{=} \int_0^\infty dr\, 4\pi r^2 r^2 \frac{1}{(4\pi D t)^{3/2}} e^{\frac{-r^2}{4Dt}}$$

$$\overset{!}{=} 6Dt \quad \sqrt{\langle \vec{r}^{\,2} \rangle} \quad \propto \sqrt{t}$$

$$P(\vec{r}, t) = \langle [\delta(\vec{r} - \vec{r}\,') \, \delta(t - t')] [\delta(\vec{r} - \vec{r}\,'') \, \delta(t - t'')] \rangle$$

$$\frac{\partial P}{\partial t} = D \nabla^2 P$$

Individual Particle:

$$r(t) = \vec{r}(0) + \int_0^t dt' \, v(t')$$

$$\delta \vec{r} = \vec{r}(t) - \vec{r}(0)$$

$$(\delta \vec{r})^2 = \delta \vec{r}(t) \cdot \delta \vec{r}(t)$$

$$\hookrightarrow \left(\int_0^t dt' \, \vec{v}(t')\right)\left(\int_0^t dt'' \, \vec{v}(t'')\right) = \int_0^t dt' \int_0^t dt'' \, \vec{v}(t') \cdot \vec{v}(t'')$$

$$\langle (\delta \vec{r}(t))^2 \rangle = \int_0^t dt' \int_0^t dt'' \underbrace{\langle v(t') \cdot v(t'') \rangle}_{k_v(\tau)}$$

<u>for $t \gg t_{relax}$:</u>

$$\langle (\delta \vec{r}(t))^2 \rangle = t \times 2 \int_0^\infty dt' \, k_v(t')$$

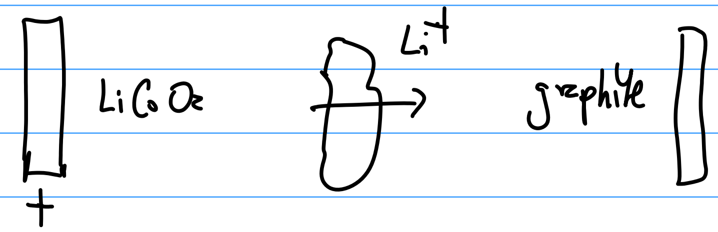
previously shown $6Dt = \langle (\delta \vec{r})^2 \rangle = t \times 2 \int_0^\infty dt' \, k_v(t)$

then $\boxed{D = \frac{1}{3} \int_0^\infty dt \, \langle \vec{v}(0) \cdot \vec{v}(t) \rangle}$

Transport Coefficient

microscopic dynamics

$D = \frac{1}{3} S_v(0)$



$$\vec{f} = q\vec{E} = -\vec{\nabla}U$$

$$m\dot{\vec{v}} = -\vec{\nabla}U + f_\sigma(t)$$

← collision.

$\langle \vec{V} \rangle = 0$ ← Normally

but now $\langle \vec{V} \rangle = \vec{V}_{drift}$.

$$\langle f_0(t) \rangle \overset{\text{Normal}}{=} 0$$

but now $\langle f_R(t) \rangle = -\gamma \vec{V}_{drift}$.

↑ viscosity.

you can show $D = \dfrac{k_B T}{\gamma}$ Einstein – Relation

$$\gamma = \beta \int_0^\infty dt \, \langle f_\sigma(0) f_\sigma(t) \rangle$$

Fluctuation Dissipation Theorem:

$$\mathcal{H}(r^N, p^N) = H_0 + \Delta H$$

assume $\quad \Delta H = -\underset{\text{force}}{f}\,\underset{\text{response}}{A}$

$$\bar{A}(0) \leftarrow \underbrace{F(r^N, p^N)}_{\text{noneq dist}} \propto e^{-\beta(H+\Delta H)}$$

non-equilibrium observable

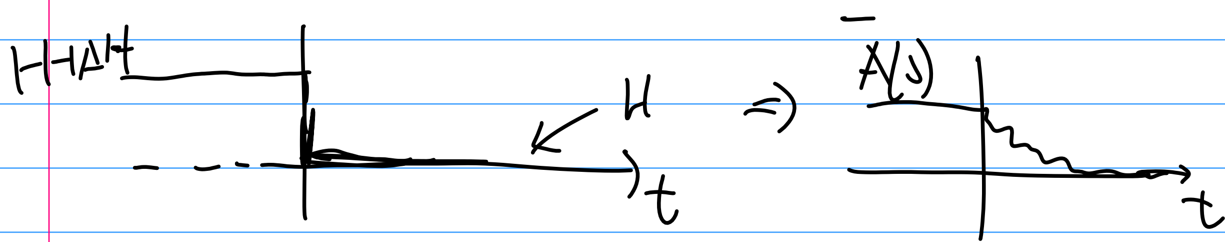
$$\bar{A}(0) = \frac{\int dr^N \int dp^N \, e^{-\beta(H+\Delta H)} A(0, r^N, p^N)}{\int dr^N \int dp^N \, e^{-\beta(H+\Delta H)}}$$

nonequilibrium

↳ short hand.
$$= \frac{\mathrm{Tr}\{e^{-\beta(H+\Delta H)} A\}}{\mathrm{Tr}\{e^{-\beta(H+\Delta H)}\}}$$

$$\langle A \rangle = \frac{\mathrm{Tr}\{e^{-\beta H} A\}}{\mathrm{Tr}\{e^{-\beta H}\}}$$

equilibrium obs



$A(t, r^N, p^N) \to$ evolves according to normal H.

$$\bar{A}(t) = \frac{Tr\{e^{-\beta(H+\Delta H)} A(t)\}}{Tr\{e^{-\beta(H+\Delta H)}\}}$$

$$\bar{A}(t) = \sum_{\substack{\text{init} \\ \text{dist}}} A(t \mid r^N, p^N)$$

$$\bar{A}(t) \cong \frac{Tr\{e^{-\beta H}(1-\beta\Delta H) A(t)\}}{Tr\{e^{-\beta H}(1-\beta\Delta H)\}}$$

For $$\frac{1}{Tr\{e^{-\beta H}(1-\beta\Delta H)\}} = \frac{1}{Tr\{e^{-\beta H}\}(1-\beta \underbrace{Tr(e^{-\beta H}\Delta H)/Tr(e^{-\beta H})}_{=\langle\Delta H\rangle})}$$

$$\cong \frac{1}{Tr\{e^{-\beta H}\}}(1+\beta\langle\Delta H\rangle)$$

$$\bar{A}(t) \approx \left[\frac{Tr\{e^{-\beta H} A(t)\}}{Tr(e^{-\beta H})} - \beta\frac{Tr\{e^{-\beta H}\Delta H\, A(t)\}}{Tr\{e^{-\beta H}\}}\right](1+\beta\Delta H)$$

$$= (\langle A\rangle - \beta\langle A\Delta H\rangle)(1+\beta\langle\Delta H\rangle)$$

$$\cong \langle A\rangle + \beta\langle A\Delta H\rangle\langle\Delta H\rangle - \beta\langle A(t)\Delta H\rangle + \mathcal{O}((\Delta H)^2)$$

If $\Delta H = -f_0 A(0)$:

then $\Delta \bar{A}(t) = \bar{A}(t) - \langle A \rangle$

$$\overset{!}{=} \beta f_0 \left(\langle A(0) A(t) \rangle - \langle A \rangle^2 \right)$$

$\langle \delta A(0) \delta A(t) \rangle$

Fluctuation Dissipation Theorem

$$\boxed{\Delta \bar{A}(t) = \beta f_0 k_A(t)}$$

$$k_A(0) = \langle (\delta A)^2 \rangle$$

$$\Delta \bar{A}(0) = \beta f_0 \langle (\delta A)^2 \rangle$$

Onsager Relation

$$\boxed{\frac{\Delta \bar{A}(t)}{\Delta \bar{A}(0)} = \frac{\beta f_0 k_A(t)}{\beta f_0 \langle (\delta A)^2 \rangle} = \frac{k_A(t)}{k_A(0)}}$$