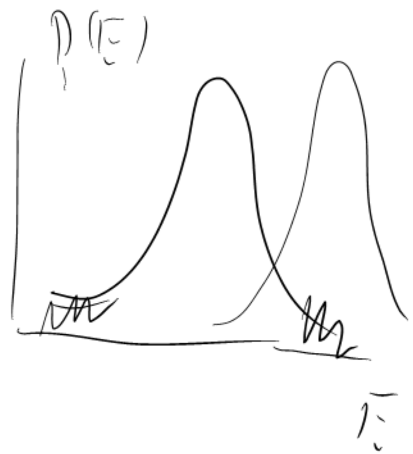
(N,V,T): $\quad C_V = T \frac{\partial S}{\partial T}\Big|_{N,V} = \underbrace{\frac{1}{T^2}\left\{\langle \mathcal{H}^2\rangle - \langle \mathcal{H}\rangle^2\right\}}_{>0}$

$$= -T \frac{\partial^2 F}{\partial T^2}\Big|_{N,V}$$

2nd derivative of potential $\longleftrightarrow$ 2nd moment of a distribution

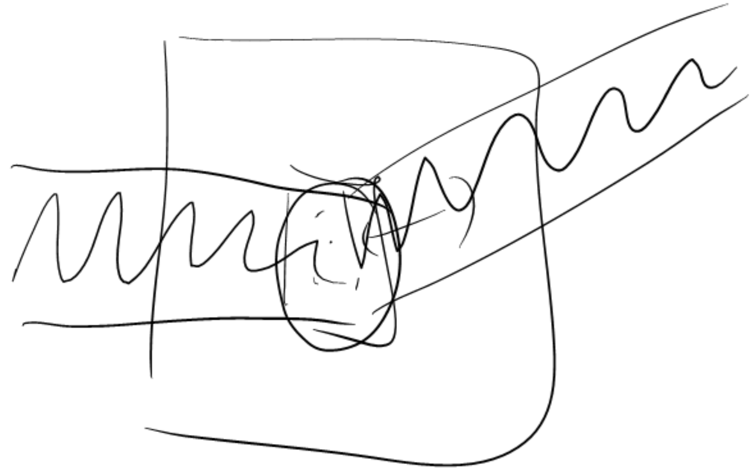
generalization:

nth deriv. $\longleftrightarrow$ nth moment



isothermal compressibility $\longleftrightarrow$ fluctuations in the particle number

$\rightarrow$ accessible via scattering



$k \to 0$

$$\propto \langle N^2\rangle - \langle N\rangle^2 \propto \kappa_T$$

Def.: $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}\Big|_{T,N}$ isothermal compr.
(ignore T-dependence)

$$= -\frac{1}{V} \frac{\partial(V,N)}{\partial(P,N)}$$

excursion: Jacobi determinants

$$(x,y) \xrightarrow[\text{invertible}]{\text{differentiable}} \big(f(x,y), g(x,y)\big)$$

volume transformation factor:

$$\det \underbrace{\begin{pmatrix} \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \\[1em] \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y} \end{pmatrix}}_{\text{Jacobi matrix}} = \left.\frac{\partial f}{\partial x}\right|_y \left.\frac{\partial g}{\partial y}\right|_x - \left.\frac{\partial f}{\partial y}\right|_x \left.\frac{\partial g}{\partial x}\right|_y$$

$$= \frac{\partial (f,g)}{\partial (x,y)} \quad \text{def.}$$

<u>prop.:</u> $$\frac{\partial (f,g)}{\partial (x,y)} = - \frac{\partial (g,f)}{\partial (x,y)} = \frac{\partial (g,f)}{\partial (y,x)}$$

<u>trick:</u> $$\boxed{\left.\frac{\partial f}{\partial x}\right|_y = \frac{\partial (f,y)}{\partial (x,y)}}$$

chain rule

$$\begin{pmatrix} x \\ y \end{pmatrix} \longrightarrow \begin{pmatrix} u \\ v \end{pmatrix} \longrightarrow \begin{pmatrix} f \\ g \end{pmatrix}$$

$$\frac{\partial(f,g)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(u,v)} \cdot \frac{\partial(u,v)}{\partial(x,y)}$$

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_{T,N} = -\frac{1}{V}\frac{\partial(V,N)}{\partial(P,N)} =$$

$$= -\frac{1}{V}\frac{\partial(V,N)}{\partial(V,\mu)}\frac{\partial(V,\mu)}{\partial(N,\mu)}\frac{\partial(N,\mu)}{\partial(P,N)} = ?$$

(i) $$\frac{\partial(V,N)}{\partial(V,\mu)} = \frac{\partial N}{\partial \mu}\bigg|_{T,V} \underset{\mu VT}{\overset{\uparrow}{=}} -\frac{\partial}{\partial \mu}\frac{\partial \Phi}{\partial \mu}\bigg|_{V,T} = -\frac{\partial^2 \Phi}{\partial \mu^2}\bigg|_{V,T}$$

$$\Phi(\mu, V, T) \,, \quad d\Phi = -S\,dT - P\,dV \underline{\underline{- N\,d\mu}}$$

(ii) $$\frac{\partial(V,\mu)}{\partial(N,\mu)} = \frac{\partial V}{\partial N}\bigg|_{\mu,T} = \frac{V}{N}$$

(iii) $$\frac{\partial(N,\mu)}{\partial(P,N)} = -\frac{\partial(\mu,N)}{\partial(P,N)} = -\frac{\partial \mu}{\partial P}\bigg|_{N,T} \underset{NPT}{\overset{\nearrow}{=}}$$

$$= -\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial N}\bigg|_{P,T}\right)\bigg|_{N,T} = -\frac{\partial}{\partial P}\left(\frac{G}{N}\right)\bigg|_{N,T} = -\frac{1}{N}\frac{\partial G}{\partial P}\bigg|_{N,T} = \underline{\underline{-\frac{1}{N}V}}$$

$$G(N,P,T) \to dG = -S\,dT + V\,dP + \mu\,dN$$

$$\mu = \frac{\partial G}{\partial N}\bigg|_{P,T} \qquad \frac{\partial G}{\partial N} = \mu = \frac{G}{N}$$

Gibbs-Duhem relation

$$\Rightarrow \kappa_T = -\frac{1}{V}\left(-\frac{\partial^2 \Phi}{\partial \mu^2}\bigg|_{V,T}\right)\frac{V}{N}\left(-\frac{V}{N}\right) =$$

$$\underline{\underline{= -\frac{V}{N^2}\frac{\partial^2 \Phi}{\partial \mu^2}\bigg|_{V,T}}}$$

Stat Phys:

$$\Phi = -T \ln Z_{GC} = -T \ln \sum_N e^{\beta\mu N} e^{-\beta F_N}$$

$$\frac{\partial \Phi}{\partial \mu} = -T \frac{\sum_N e^{\beta\mu N} e^{-\beta F_N} \beta N}{\sum_N e^{\beta\mu N} e^{-\beta F_N}} =$$

$$= - \frac{\sum_N e^{\beta\mu N} e^{-\beta F_N} N}{\sum_N e^{\beta\mu N} e^{-\beta F_N}} = - \langle N \rangle$$

$$\frac{\partial^2 \Phi}{\partial \mu^2} = - \frac{1}{\left(\sum_N e^{\beta\mu N} e^{-\beta F_N}\right)^2} \left\{ \left(\sum_N e^{\beta\mu N} e^{-\beta F_N} N \beta N\right) \times \right.$$

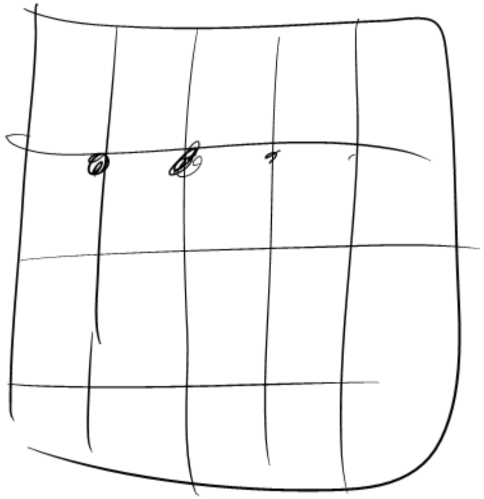
$$\left(\sum_N e^{\beta\mu N} e^{-\beta F_N}\right) - \left(\sum_N e^{\beta\mu N} e^{-\beta F_N} N\right) \times$$

$$\left. \times \left(\sum_N e^{\beta\mu N} e^{-\beta F_N} \beta N\right) \right\} =$$

$$= -\beta \left\{ \langle N^2 \rangle - \langle N \rangle^2 \right\}$$

$$\boxed{\kappa_T = + \frac{1}{T} \frac{V}{N^2} \left\{ \langle N^2 \rangle - \langle N \rangle^2 \right\}} > 0$$

"Magnetic" Systems



lattice with sites i

on each site: spin variable S_i

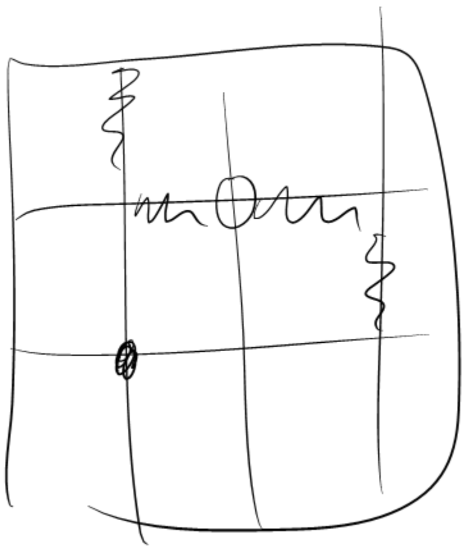
→ Ising spins: $S_i = \pm 1$ $\qquad S_i^2 = 1$

<u>XY</u> spins: $\vec{S}_i = \begin{pmatrix} \cos\varphi \\ \sin\varphi \end{pmatrix}$ $\qquad \vec{S}_i^{\,2} = 1$

Heisenberg spins: $\vec{S}_i$ 3dimensional

$$\vec{S}_i^{\,2} = 1$$

lattice gas: (binary alloy: A-atom
B-atom)



$$c_i = \begin{cases} 1 & \text{A-atom} \\ 0 & \text{B-atom} \end{cases}$$

$$\mathcal{H} = \mathcal{H}(\{c_i\}) = \mathcal{H}(\{S_i\})$$

$$S_i = (2c_i - 1) \rightarrow c_i = \frac{1}{2}(S_i + 1)$$

nn interactions

$$\mathcal{H} = \sum_{\langle ij \rangle} \Big(\underline{V_{AA}}\, c_i c_j + \underline{V_{BB}}\, (1-c_i)(1-c_j) + \underline{V_{AB}} \big[c_i (1-c_j) + (1-c_i) c_j \big] \Big)$$

$\langle ij \rangle$ nearest neighbor pairs

V_{AA}: AA bond

$$= \ldots = \underbrace{\sum_{\langle ij \rangle} \big[(-J)\, S_i S_j \big] - \underset{\sim}{H_0} \sum_i S_i + \text{const.}}$$

Ising systems:

$$\mathcal{H}(\{S_i\}) = -J \sum_{\langle ij \rangle} S_i S_j - \underline{H \sum_i S_i}$$

exchange constant

magnetic field

$\sum_i S_i = M$ magnetization

generalize: $\mathcal{H}(\{S_i\}) = \mathcal{H}_0(\{S_i\}) - H \sum_i S_i$

partition fct. in the $H = \text{const.}$, $T = \text{const.}$

ensemble: $$Z = \sum_{\{S_i\}} \exp[-\beta \mathcal{H}_0] \exp[+\beta H \textstyle\sum_i S_i]$$

↳ independent of H!

→ free energy:

$$F = -\frac{1}{\beta} \ln Z = F(\beta, H) = F(T, H)$$

$$-\frac{\partial F}{\partial H} = +T \frac{1}{Z} \sum_{\{S_i\}} e^{-\beta \mathcal{H}_0} e^{\beta H M} \beta M = \langle M \rangle$$

$$\Rightarrow \boxed{dF = -S\,dT - M\,dH} \qquad \begin{pmatrix} dV = 0 \\ dN = 0 \end{pmatrix}$$

$$\boxed{d\tilde{F} = -S\,dT + H\,dM}$$

$$\tilde{F} = F + MH$$

(magnetic)
susceptibility

$$-\frac{\partial^2 F}{\partial H^2} = \frac{\partial}{\partial H}\Big(\underbrace{-\frac{\partial F}{\partial H}}_{M}\Big) = \frac{\partial M}{\partial H} =: \underline{\underline{\chi N}}$$

$N \equiv$ # lattice sites

$$F = -T \ln Z \qquad \Rightarrow -\frac{\partial F}{\partial H} = -T \frac{1}{Z} \sum_{\{S_i\}} e^{-\beta \mathcal{H}_0} e^{\beta H M} \beta M$$

$$= \frac{1}{Z} \sum_{\{S_i\}} e^{-\beta \mathcal{H}_0} e^{\beta H M} M$$

$$-\frac{\partial^2 F}{\partial H^2} = -\frac{1}{Z^2} \left(\sum_{\{S_i\}} e^{-\beta \mathcal{H}_0} e^{\beta H M} \beta M \right) \left(\sum_{\{S_i\}} e^{-\beta \mathcal{H}_0} e^{\beta H M} M \right)$$

$$+ \frac{1}{Z} \left(\sum_{\{S_i\}} e^{-\beta \mathcal{H}_0} e^{\beta H M} \beta M^2 \right) = \beta \left(\langle M^2 \rangle - \langle M \rangle^2 \right)$$

$$\chi = \frac{1}{NT}\left[\langle M^2\rangle - \langle M\rangle^2\right] > 0 \quad \text{intensive}$$

$$\chi_0 = 0 \qquad \text{Ising-paramagnet}$$

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

1d Ising model