$$\lim_{N\to\infty} \frac{N(i)}{N} = P(i)$$

$$\langle F(i)\rangle = \sum_i F(i)P(i)$$

$$S = \log M = -\sum_i P(i)\log[P(i)] = -\int P(p,x)\log[P(p,x)]\,dp\,dx$$

$$S_{\substack{max\\ for\ 2}} = n\log 2 \qquad (\log 2 \to 1 \text{ byte})$$

$$E = \frac{3}{2}k_B t_k = \frac{3}{2}T \qquad \left(k_B = 1{,}4.10^{-23}\ J/K\right)$$

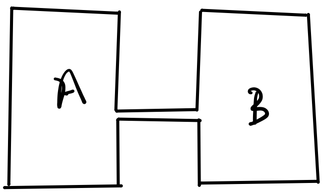
$$S = \frac{1}{k_B} S_{Carnot}$$

$$S(E) = -\sum_i P(i,E)\log[P(i,E)]$$

$$\Delta E = \frac{\partial E}{\partial S}\Delta S = T.\Delta S$$

$dE = T.dS$

as E increases, S increases



1st law $dE_A = -dE_B$ $\qquad dE_A = T_A . dS_A$

2nd law $dS_A + dS_B > 0$ $\qquad dE_B = T_B . dS_B$

$dE_A + dE_B = 0$, $T_A dS_A + T_B dS_B = 0 \Rightarrow dS_B = -\frac{T_A}{T_B} dS_A$

$dS_A + dS_B > 0 \Rightarrow (T_B - T_A) dS_A > 0$

$dS_A > 0$

$dE_A > 0$

$dE_B < 0$

$$\cancel{A}\ P_i = \frac{n_i}{N}$$

$$NP_i = n_i$$

Number of arrangements: $\dfrac{N!}{\prod_i n_i!}$

$N! \simeq N^N e^{-N}$ when N is large

$\Bigg\}$ Number of arrangements $\dfrac{N^N}{\prod_i n_i^{n_i}} = C$

$$\log C = N\log N - \sum_i n_i \log n_i = N \log N - \sum_i N p_i (\log p_i + \log N) = -N \sum_i p_i \log p_i = NS$$

maximize S in order to maximize number of arrangements.

Using Lagrange Multipliers

$$-S(p_i) = +\sum_i p_i \log(p_i) = F(p_i)$$

$$G_1 : \sum_i p_i - 1 = 0$$

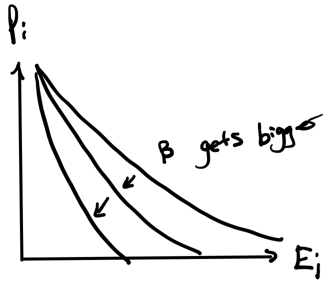
$$G_2 : \sum_i E_i p_i - \langle E \rangle = 0$$

$$\sum_i p_i \log p_i + \alpha\Big[\sum_i p_i - 1\Big] + \beta\Big[\sum_i p_i E_i - \langle E \rangle\Big] = F'(p_i)$$

$$\nabla F'(p_i) = \log p_i + 1 + \alpha + \beta E_i = 0$$

$$\log p_i = -(1+\alpha) - \beta E_i$$

$$p_i = e^{-(1+\alpha)} e^{-\beta E_i} = \frac{1}{z} e^{-\beta E_i} \quad \left(z = e^{(1+\alpha)}\right)$$



* the greater the β, the less the $\langle E \rangle$

Constraints:

$$\sum_i p_i = 1 \longrightarrow \frac{1}{z}\sum_i e^{-\beta E_i} = 1 \Longrightarrow \sum_i e^{-\beta E_i} = z(\beta) \Longrightarrow \frac{\partial z(\beta)}{\partial \beta} = -\sum_i e^{-\beta E_i} E_i$$

$$\frac{1}{z}\sum_i e^{-\beta E_i} E_i = -\frac{1}{z}\frac{\partial z}{\partial \beta} = E = -\frac{\partial \log z}{\partial \beta}$$

$$S = -\sum_i p_i \log p_i = -\sum_i \frac{1}{Z} e^{-\beta E_i} \log\left[\frac{1}{Z} e^{-\beta E_i}\right] = \sum_i \frac{1}{Z} e^{-\beta E_i} \left(\beta E_i + \log Z\right)$$

$$= \beta \sum_i p_i E_i + \frac{1}{Z} \log Z \sum_i e^{-\beta E_i} = \beta E + \log Z$$

$$dS = E d\beta + \beta dE + \frac{d \log Z}{d\beta} d\beta = \beta dE \implies T = \frac{1}{\beta} \quad \left(\beta = \frac{1}{k_B T}\right)$$

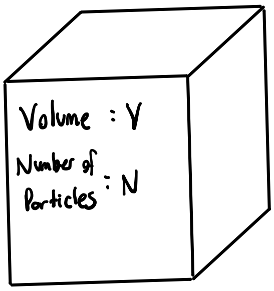
$$P_i = \frac{1}{Z} e^{-\beta E_i}$$

$$Z = \sum_i e^{-\beta E_i}$$

$$E = -\frac{\partial \log Z}{\partial \beta}$$

$$T = \frac{1}{\beta}$$

$$S = \beta E + \log Z$$



states

$x_1 \cdots x_{3N}$

$p_1 \cdots p_{3N}$

$$Z = \int_{-\infty}^{\infty} e^{-\beta \sum_{n=1}^{3N} \frac{p_n^2}{2m}} d^{3N}x \, d^{3N}p = \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \sum_{n=1}^{3N} p_n^2} d^{3N}x \, d^{3N}p \quad \left(\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p_1^2} dp_1 \, e^{-\frac{\beta}{2m} p_2^2} dp_2 \cdots\right)$$

$$= \frac{V^N}{N!} \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} = \left(\frac{Ve}{N}\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} = \left(\frac{e}{\rho}\right)^N \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}}$$

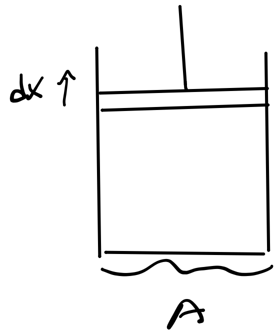
$$\log Z = N\left[\log\left(\frac{e}{\rho}\right) + \frac{3}{2} \log\left(\frac{2m\pi}{\beta}\right)\right] = N\left[1 - \log \rho + \frac{3}{2} \log\left(\frac{2m\pi}{\beta}\right)\right] = \cdots\cdots - \frac{3N}{2} \log \beta$$

$$-\frac{\partial \log Z}{\partial \beta} = \frac{3N}{2\beta} = \frac{3}{2} N T k_B = E$$

$$S = \beta E + \log Z = \frac{E}{T} + \log Z \Longrightarrow \underbrace{E - TS}_{} = -T\log Z$$

$A =$ Helmholtz free energy

$$\left.\frac{\partial E}{\partial V}\right|_S = \left.\frac{\partial E}{\partial V}\right|_T - \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T$$



$$dE = -PA\,dx = -P\,dV \Longrightarrow \underbrace{\frac{\partial E}{\partial V} = -P}_{}$$

means P and V are conjugate thermodynamic parameters

$$\left.\frac{\partial E}{\partial V}\right|_S = \left.\frac{\partial E}{\partial V}\right|_T - \left.\frac{\partial E}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T \Longrightarrow P = -\left.\frac{\partial E}{\partial V}\right|_T + \left.\frac{\partial S}{\partial V}\right|_T T \Longrightarrow P = -\left.\frac{\partial}{\partial V}(E - TS)\right|_T$$

$$= -\left.\frac{\partial A}{\partial V}\right|_T$$

$$= T\left.\frac{\partial \log Z}{\partial V}\right|_T$$

$$Z = \int e^{-\beta\frac{p^2}{2m}} d^{3N}p\, d^{3N}x = \frac{V^N}{N!} f(\beta) \Longrightarrow \log Z = N\log V - \log N! + \log f(\beta)$$

$f(\beta)$

$$\frac{\partial \log Z}{\partial V} = \frac{N}{V} \Longrightarrow PV = NT \Longrightarrow P = \rho T$$

by def.

$$\left\langle (x - \langle x\rangle)^2 \right\rangle = \left\langle x^2 - 2x\langle x\rangle + \langle x\rangle^2 \right\rangle = \langle x^2\rangle - \langle x\rangle^2 = (\Delta x)^2$$

$$(\Delta E)^2 = \langle E^2\rangle - \langle E\rangle^2 = \sum \frac{1}{Z} e^{-\beta E_i} E^2 - \left[\frac{1}{Z}\frac{\partial Z}{\partial b}\right]^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\langle E\rangle$$

$$= T^2\frac{\partial}{\partial T}\langle E\rangle$$

$$= C_V T^2 \, (k_B)$$

fluctuation

$$E = \sum_n \frac{p^2}{2M} + \sum_{n>m} U(|x_n - x_m|)$$

$$\int U(|x_1 - x_2|)\, d^3x_1\, d^3x_2 = V U_0$$

$$\int U(|x|)\, d^3x = U_0 \sim VU$$

$$Z = \int \frac{1}{N!} e^{-\beta \sum_n \frac{p^2}{2M}} e^{-\beta \sum_{n>m} U(|x_n - x_m|)} d^{3N}x\, d^{3N}p = \int \frac{e^{-\beta \sum_n \frac{p_n^2}{2m}}}{N!} d^{3N}p \int e^{-\beta \sum_{n>m} U(|x_n - x_m|)} d^{3N}x$$

$$= \int \frac{V^N}{N!} e^{-\beta \sum_n \frac{p_n^2}{2m}} d^{3N}p \int \frac{e^{-\beta \sum_{n>m} U(|x_n - x_m|)}}{V^N} d^{3N}x = Z_0 \int \frac{e^{-\beta \sum_{n>m} U(|x_n - x_m|)}}{V^N} d^{3N}x$$

$$\int \frac{e^{-\beta \sum_{n>m} U(|x_n - x_m|)}}{V^N} d^{3N}x = \int \frac{1 - \beta \sum_{n>m} U(|x_n - x_m|)}{V^N} d^{3N}x = 1 - \beta \int \frac{\sum_{n>m} U(|x_n - x_m|)}{V^N} d^{3N}x$$

$$= 1 - \beta \int \frac{U(|x_1 - x_2|)}{V^N} d^3x_1\, d^3x_2\, d^{3N-6}x = 1 - \frac{\beta N^2}{2V} U_0$$

$$\Downarrow$$

$$Z = Z_0 \left(1 - \frac{\beta N^2}{2V} U_0\right)$$

$$\log Z = \log Z_0 + \log\left(1 - \frac{\beta N^2}{2V} U_0\right) = \log Z_0 - \frac{\beta N^2}{2V} U_0$$

$$\left(\log(1-x) \sim -x\right)$$

$$E = -\frac{\partial \log Z}{\partial \beta} = \frac{3}{2} NT + \frac{N^2}{2V} U_0 = \frac{3}{2} NT + N \frac{\rho}{2} U_0 = N\left[\frac{3}{2} T + \frac{\rho}{2} U_0\right]$$

Energy per particle

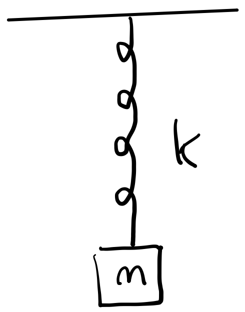
$$P = -\frac{\partial A}{\partial V}\Big|_T = T\,\frac{\partial \log Z}{\partial V}\Big|_T = \rho T + \frac{1}{2}\rho^2 U_0$$

(when $\rho U_0 \ll T$)

$$dE = TdS - PdV$$
$$\quad dQ + dW$$

$$\frac{3}{2}Nk_BT = \frac{1}{2}mv^2 \Longrightarrow v^2 = \frac{3Nk_BT}{m}$$

$$\frac{1}{m}\frac{\partial P}{\partial \rho} = \frac{1}{m}\frac{\partial}{\partial \rho}(\rho k_B T) = \frac{k_BT}{m} = c^2$$



$$Z = \int e^{-\beta\frac{p^2}{2m}}\, e^{-\beta\frac{kx^2}{2}}\, dp\,dx = \int e^{-\beta\frac{p^2}{2m}}dp \int e^{-\beta\frac{kx^2}{2}}dx$$

$$\left(\frac{\beta p^2}{2m} = q^2 \Longrightarrow p = q\sqrt{\frac{2m}{\beta}}\right) \quad \left(\frac{\beta kx^2}{2} = y^2 \Longrightarrow x = y\sqrt{\frac{2}{k\beta}}\right)$$

$$\sqrt{\frac{2m}{\beta}}\int e^{-q^2}dq\,\sqrt{\frac{2}{k\beta}}\int e^{-y^2}dy = \frac{2\pi}{\beta}\sqrt{\frac{m}{k}} = \frac{2\pi}{\omega}\frac{1}{\beta}$$

$$\log Z = \log\left(\frac{2\pi}{\omega}\right) - \log\beta$$

$$-\frac{\partial \log Z}{\partial \beta} = \frac{1}{\beta} = T = E$$

For a Quantum Oscillator

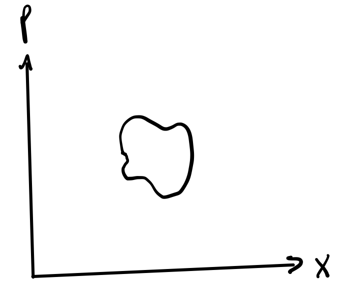
$$Z = \sum_n e^{-\beta n\hbar\omega} = \sum_n \left(e^{-\beta\hbar\omega}\right)^n = \sum_n x^n = \frac{1}{1-x} = \frac{1}{1-e^{-\beta\hbar\omega}}$$

$$E = -\frac{\partial \log Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \simeq \frac{\hbar\omega}{\beta\hbar\omega} = \frac{1}{\beta} = T$$

classical assumption of low β

$\beta\hbar\omega > 1$ quantum
$\beta\hbar\omega < 1$ classical

$\hbar\omega = T \longrightarrow$ crossover occurs



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

# of ups : n
# of downs : m

$n + m = N$

μ : magnetic moment (how strong it interacts)

H : magnetic field

$$E = (n-m)\mu H \qquad \left(x = e^{-\beta\mu H},\ y = e^{\beta\mu H}\right)$$

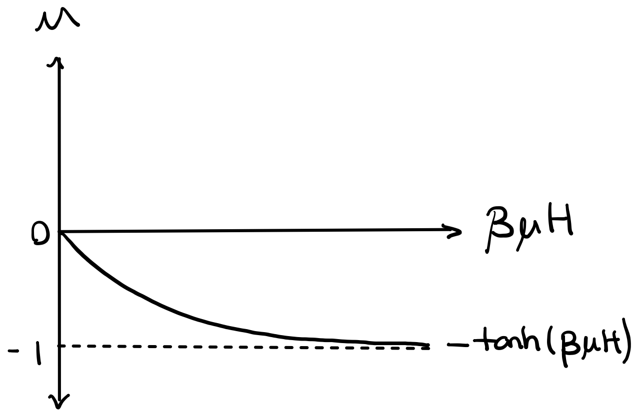
$$Z = \sum_{nm} e^{-\beta(n-m)\mu H} \Longrightarrow \sum_{n} \frac{N!}{n!(N-n)!} x^n y^{N-n} = (x+y)^N$$

$$\left(e^{-\beta\mu H} + e^{\beta\mu H}\right)^N = \left(\frac{e^{-\beta\mu H} + e^{\beta\mu H}}{2}\right)^N 2^N = 2^N \cosh^N \beta\mu H$$

$$\langle M \rangle \equiv \frac{\langle n-m \rangle}{N}$$

$$\langle E \rangle \equiv N\mu H \langle M \rangle$$

$$-\frac{\partial \log Z}{\partial \beta} = -N\mu H \tanh(\beta\mu H) = E \Longrightarrow M = -\tanh(\beta\mu H)$$



$\beta \to \infty \quad M \to -1$ (down)

$\beta \to 0 \quad M \to 0$

$$E = -J\sigma(1)\sigma(2) \Longrightarrow E = -J\sum_n \sigma(n)\sigma(n+1)$$

Symmetry $\longrightarrow$ doesn't change the energy

$$E = \mu H \sigma = -J\sigma$$

$$Z = \sum e^{\beta J \sigma} = e^{\beta J} + e^{-\beta J} = 2\cosh(\beta J)$$

$$E = -\frac{\partial \log Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{2\cosh(\beta J)} \cdot 2J\sinh(\beta J) = -J\tanh(\beta J)$$

$$\langle \sigma \rangle = \tanh(\beta J)$$

$$E = -J\sum_i \sigma_i \sigma_{i+1} = -J\sum_i \mu_i$$

$$Z = \sum_\sigma e^{\beta J \sum_i \sigma_i \sigma_{i+1}} = 2\sum_\mu e^{\beta J \sum_i \mu_i} = 2(2\cosh(\beta J))^{N-1}$$

$$\sigma_1\sigma_2 = \mu_1 \,,\quad \sigma_2\sigma_3 = \mu_2 \ldots$$

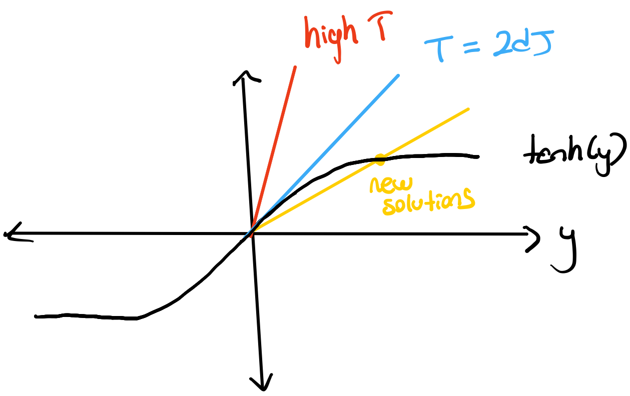
$$\langle \mu \rangle = \langle \sigma_i \sigma_{i+1} \rangle = \tanh(\beta J)$$

$$\langle \underbrace{\sigma_i \, \sigma_{i+1}}_{\mu_1} \underbrace{\sigma_{i+1} \, \sigma_{i+2}}_{\mu_2} \cdots \sigma_{i+n} \rangle = \langle \mu_1 \mu_2 \cdots \mu_{n-1} \rangle = [\tanh(\beta J)]^{n-1}$$

2d neighbors

$$E = -J\sigma \sum_{\text{neighbor}} \sigma = -2dJ\sigma\bar{\sigma}$$

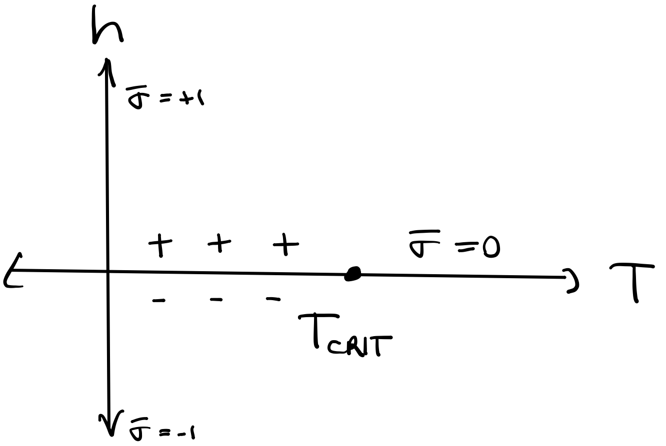
$$\left.\begin{aligned} \bar{\sigma} &= \tanh(2\beta d J \bar{\sigma}) \\ \frac{y}{2\beta d J} &= \frac{Ty}{2dJ} = \tanh(y) \end{aligned}\right\}$$

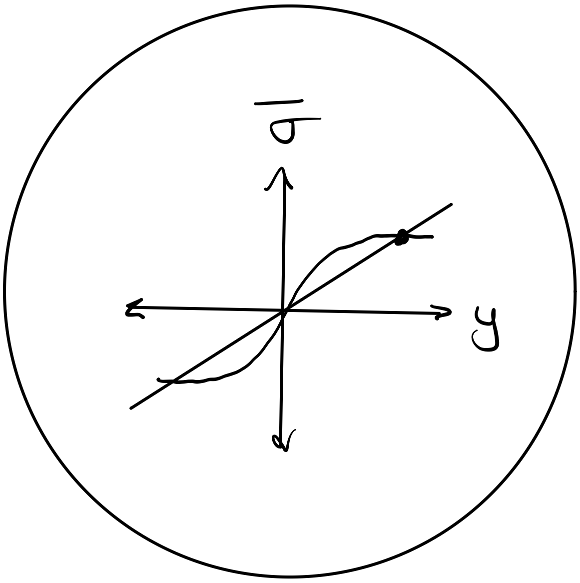


$$E = -J \sum_{\text{links}} \sigma_i \sigma_j + h \sum_{\text{sites}} \sigma_i = \overbrace{-2dJ\bar{\sigma}\sigma + h\sigma}^{\text{single site}}$$

$$\bar{\sigma} = \tanh\left[\left(2dJ\bar{\sigma} + h\right)\beta\right]$$

$$\frac{yT}{2dJ} = \tanh\left(y - \beta h\right) \Rightarrow T = 2dJ \text{ critical temperature}$$





Liquid - Gas

$\sigma = -1$ no particle

$\sigma = +1$ there is a particle

$$\frac{1+\bar{\sigma}}{2} = \rho$$