Zahra Shivji

Ch/ChE 164 Winter 2024
Homework Problem Set #6
Due Date: Thursday, February 29, 2024 @ 11:59pm PT
Out of 100 Points

Project - Work on Question 1

1. Consider a liquid at temperature T in equilibrium with its vapor (at pressure p). Assume that the liquid-vapor interface is planar and that the vapor can be regarded as ideal.

(i) *(20 points)* Use the Maxwell-Boltzmann distribution to find the average number of vapor molecules that hit the interface per unit area per unit time.

(ii) *(10 points)* If a fraction ϕ of these molecules are bounced back, find the rate of evaporation of the liquid, *i.e.*, the number of molecules that evaporate from the liquid per unit area per unit time.

2. *(20 points)* Derive the adsorption isotherm for a 2-component ideal gas containing species A and B. Assume that each adsorption site can only be singly occupied. The adsorption energy for species A is $-\varepsilon_A$ and that for species B is $-\varepsilon_B$. Express your result in terms of the partial pressures of each component.

3. For the noninteracting Ising model, the joint probability for the system factorizes into a product of the probability for each spin, i.e., $P(\{s\}) = \prod_i p_i(s_i)$.

(i) *(5 points)* Show that the Gibbs entropy is now

$$S = -k \sum_i \sum_{s_i} p_i(s_i) \ln p_i(s_i) \tag{1}$$

(ii) *(5 points)* Introducing the order parameter (average spin) $m_i = \langle s_i \rangle$, show that the variational free energy is

$$G = -\sum_i h_i m_i + kT \sum_i \left(\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right) \tag{2}$$

(iii) *(10 points)* Show that minimization of this free energy yields the same equation of state as obtained in class by directly working with the partition function. Also show that the minimized free energy is the same as obtained in class using the partition function.

4. For the 1-dimensional Ising model with periodic boundary condition, the Hamiltonian is given by

$$H = -K(s_1 s_2 + s_2 s_3 + \cdots + s_N s_1) - h \sum_{i=1}^{N} s_i \tag{3}$$

Use the transfer matrix method to obtain an exact solution in the limit of large N. In particular,

(i) *(10 points)* Show that the partition function is given by

$$Z = \mathrm{Tr}(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N \approx \lambda_+^N \tag{4}$$

with the transfer matrix

$$\mathbf{T} = \begin{pmatrix} e^{\beta K + \beta h} & e^{-\beta K} \\ e^{-\beta K} & e^{\beta K - \beta h} \end{pmatrix} \tag{5}$$

and λ_+ the larger of the two eigenvalues of the transfer matrix, λ_+ and λ_-.

(ii) *(10 points)* Show that the eigenvalues are

$$\lambda_\pm = e^{\beta K} \cosh(\beta h) \pm \sqrt{e^{2\beta K} \sinh^2(\beta h) + e^{-2\beta K}} \tag{6}$$

(iii) *(10 points)* Examine and comment on the behavior of entropy and energy at $T = 0$ and $T = \infty$.

(iv) *(**Bonus 15 points**)* Show that the spin-spin correlation function at zero external field is given by

$$\langle s_i s_{i+r} \rangle = \frac{\lambda_+^{N-r}\lambda_-^r + \lambda_-^{N-r}\lambda_+^r}{\lambda_+^N + \lambda_-^N} \approx \left(\frac{\lambda_-}{\lambda_+}\right)^r \equiv \mathrm{e}^{-r/\xi} \tag{7}$$

with the correlation length

$$\xi = \left[\ln\left(\frac{\lambda_+}{\lambda_-}\right)\right]^{-1} = -\frac{1}{\ln\tanh(\beta K)} \tag{8}$$

For Problem 4, you may consult any reference materials, including books and online resources. However, the work you write down must reflect your own understanding.

ideal v

↓↑

liq

(1) Consider a liquid at temperature T in equilibrium with its vapor (at pressure p). Assume that the liquid-vapor interface is planar and that the vapor can be regarded as ideal.

(i) *(20 points)* Use the Maxwell-Boltzmann distribution to find the average number of vapor molecules that hit the interface per unit area per unit time.

(ii) *(10 points)* If a fraction ϕ of these molecules are bounced back, find the rate of evaporation of the liquid, *i.e.*, the number of molecules that evaporate from the liquid per unit area per unit time.

i) Maxwell-Boltzmann distribution

avg flux $\rightsquigarrow \langle N_x \rangle = \rho \langle v_x \rangle$ 1D only

$$f(\bar{p}) = \left(\frac{1}{2\pi m kT}\right)^{3/2} e^{-p^2/2mkT} \rightarrow g(\bar{v})\,d\bar{v} = f(\bar{p})\,d\bar{p}$$

$$g(\bar{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m\bar{v}^2/2kT}$$

gaussian $\int_0^\infty e^{-ax^2}dx^2 = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

$$\langle v_x \rangle = \int v_x\, g(\bar{v})\,d\bar{v}$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \int_0^\infty \int_0^\infty v_x\, e^{-\frac{m}{2kT}(v_x^2 + v_y^2 + v_z^2)}\,dv_x\,dv_y\,dv_z$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT\pi}{m}\right)^{1/2} \int_0^\infty \int_0^\infty v_x\, e^{-\frac{m}{2kT}(v_x^2 + v_y^2)}\,dv_x\,dv_y$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT\pi}{m}\right) \int_0^\infty v_x\, e^{-\frac{m}{2kT}(v_x^2)}\,dv_x$$

$\int_0^\infty x e^{-ax^2}dx = \frac{1}{2a}$

$$\langle v_x \rangle = \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{kT}{m}\right) \left(\frac{2kT\pi}{m}\right)$$

$$\boxed{\langle N_x \rangle = \rho \left(\frac{kT}{2\pi m}\right)^{1/2}}$$

ii) $\phi \langle N_x \rangle$ bounce back

↪ $(1-\phi)\langle N_x \rangle$ penetrate liq

@ eq: $N_{evap} = (1-\phi)\langle N_x \rangle$

$$\boxed{N_{evap} = (1-\phi)\rho\left(\frac{kT}{2\pi m}\right)^{1/2}}$$

2 . *(20 points)* Derive the adsorption isotherm for a 2-component ideal gas containing species A and B. Assume that each adsorption site can only be singly occupied. The adsorption energy for species A is $-\varepsilon_A$ and that for species B is $-\varepsilon_B$. Express your result in terms of the partial pressures of each component. non-interacting

N sites

$$Q = Q_A Q_B = \binom{N}{n_A}\binom{N-n_A}{n_B} q_{ad}^{A}\, q_{ad}^{B}, \quad q_{ad} = \exp(-n\beta\epsilon)$$

$$Q = \frac{N!}{n_A!\,\cancel{(N-n_A)!}} \frac{\cancel{(N-n_A)!}}{n_B!\,(N-n_A-n_B)!} e^{n_A\beta\epsilon_A} e^{n_B\beta\epsilon_B}$$

$$\theta_A = n_A/N, \quad \theta_B = n_B/N, \quad \theta_A + \theta_B = \theta = n/N$$

$$F = -kT\ln Q$$

$$\ln Q = n_A \beta \epsilon_A + n_B \beta \epsilon_B + N\ln N - \cancel{N} - n_A \ln n_A + \cancel{n_A} - n_B \ln n_B + \cancel{n_B} - (N-n_A-n_B)\ln(N-n_A-n_B) \cancel{+N} \cancel{-n_A} \cancel{-n_B}$$

$$\mu_{ad_A} = \frac{\delta F}{\delta n_A} = -kT\left[\beta\epsilon_A - \ln n_A \cancel{-1} + \ln(N-n_A-n_B) \cancel{+1}\right]$$

$$\mu_{ad_A} = -\epsilon_A - kT\ln\left(\frac{N-n_A-n_B}{n_A}\right) = -\epsilon_A + kT\ln\left(\frac{\theta_A}{1-\theta_A-\theta_B}\right)$$

$$\mu_{ad_B} = -\epsilon_B + kT\ln\left(\frac{\theta_B}{1-\theta_A-\theta_B}\right)$$

@ equilibrium, $\mu_{ad} = \mu_{gas} = kT\ln\frac{\rho\Lambda^3}{q^3}$

$$e^{\ln\left[\frac{\theta_A}{1-\theta_A-\theta_B}\right]} = e^{\beta\epsilon_A + \beta\mu_{gas}}$$

$P = \rho kT$

$$\frac{\theta_A}{1-\theta_A-\theta_B} = e^{\beta\epsilon_A} \cdot \frac{\rho_A \Lambda_A^3}{(q_{ad}^A)^3} = \underbrace{\frac{e^{\beta\epsilon_A}}{kT}}_{K_A} \cdot P_A$$

by analogy $K_B \rightsquigarrow \frac{e^{\beta\epsilon_B}}{kT}$

$$\boxed{\theta_A = \frac{K_A P_A}{1+K_A P_A + K_B P_B}}$$

$$\boxed{\theta_B = \frac{K_B P_B}{1+K_A P_A + K_B P_B}}$$

$$\theta = \theta_A + \theta_B$$

$$\boxed{\theta = \frac{K_A P_A + K_B P_B}{1+K_A P_A + K_B P_B}}$$

3

For the noninteracting Ising model, the joint probability for the system factorizes into a product of the probability for each spin, i.e., $P(\{s\}) = \prod_i p_i(s_i)$.

(i) *(5 points)* Show that the Gibbs entropy is now

$$S = -k \sum_i \sum_{s_i} p_i(s_i) \ln p_i(s_i) \tag{1}$$

i) $P(\{s\}) = \prod_i P_i(s_i)$ probability of full spin state of sys.

spins independent & have same probability distr.

entropy of one state s_i

$$S_i = -k \sum_{s_i} p_i(s_i) \ln p_i(s_i)$$

$$S = \sum_i S_i$$ → entropy extensive

$$\boxed{S = -k \sum_i \sum_{s_i} p_i(s_i) \ln p_i(s_i)}$$

(ii) *(5 points)* Introducing the order parameter (average spin) $m_i = \langle s_i \rangle$, show that the variational free energy is

$$G = -\sum_i h_i m_i + kT \sum_i \left(\frac{1+m_i}{2} \ln \frac{1+m_i}{2} + \frac{1-m_i}{2} \ln \frac{1-m_i}{2} \right) \tag{2}$$

ii)

$P_i^+ + P_i^- = 1$

$$m_i = \langle s_i \rangle = \sum_{s_i} s_i P(s_i) = P_i^+ - P_i^- \quad \left\{ s \text{ only } + \text{ or } - \right.$$

$$P_i^+ = \frac{1+m_i}{2}, \quad P_i^- = \frac{1-m_i}{2}$$

$$G = \langle E \rangle - TS$$

$$\langle E \rangle = -\left\langle \sum_i h_i s_i \right\rangle = -\sum_i h_i \langle s_i \rangle = -\sum_i h_i m_i$$

$$G = -\sum_i^N h_i m_i + kT \sum_i^N \sum_{s_i} P_i(s_i) \ln P_i(s_i)$$

$$\boxed{G = -\sum_i^N h_i m_i + kT \sum_i^N \left[\left(\frac{1+m_i}{2}\right) \ln\left(\frac{1+m_i}{2}\right) + \left(\frac{1-m_i}{2}\right) \ln\left(\frac{1-m_i}{2}\right) \right]}$$

iii) *(10 points)* Show that minimization of this free energy yields the same equation of state as obtained in class by directly working with the partition function. Also show that the minimized free energy is the same as obtained in class using the partition function.

$$0 = \frac{\delta G}{\delta m_i} = -\sum_i^N h_i + kT \sum_i^N \left[\frac{1}{2} \ln\left(\frac{1+m_i}{2}\right) + \cancel{\frac{1}{2}} - \frac{1}{2} \ln\left(\frac{1-m_i}{2}\right) - \cancel{\frac{1}{2}} \right]$$

$$h_i = \frac{kT}{2} \ln\left(\frac{1+m_i}{1-m_i}\right) \rightsquigarrow e^{2h_i\beta} = \frac{1+m_i}{1-m_i}$$

$$(1-m_i)\, e^{2h_i\beta} = 1+m_i$$

$$\frac{e^{-h_i\beta}}{e^{-h_i\beta}} \cdot \frac{e^{2h_i\beta}-1}{e^{2h_i\beta}+1} = m_i = \frac{e^{h_i\beta}-e^{-h_i\beta}}{e^{h_i\beta}+e^{-h_i\beta}}$$

$$\boxed{m_i = \tanh(h_i\beta)}$$

plug m_i back into G:

$$G_{min} = -\sum_i^N h_i \tanh(h_i\beta) + kT \sum_i^N \left[\frac{1+\tanh(h_i\beta)}{2} \ln\left(\frac{1+\tanh(h_i\beta)}{2}\right) + \frac{1+\tanh(h_i\beta)}{2} \ln \frac{1+\tanh(h_i\beta)}{2} \right]$$

simplifies to ...

$$\boxed{G_{min} = -kT \sum_i \ln\left(e^{\beta h_i} + e^{-\beta h_i}\right)}$$

$$\ln\left(\frac{1+m_i}{2}\right) = \ln\left[\frac{e^{2h_i\beta}\cancel{+1}\,\cancel{+e^{2h_i\beta}-1}}{\cancel{2}(e^{2h_i\beta}+1)}\right] = \ln(e^{2h_i\beta}) - \ln(e^{2h_i\beta}+1)$$

$$\left(\frac{1+m_i}{2}\right)\ln\left(\frac{1+m_i}{2}\right) + \left(\frac{1-m_i}{2}\right)\ln\left(\frac{1-m_i}{2}\right)$$

$$= \left(\frac{e^{2h_i\beta}}{1+e^{2h_i\beta}}\right)\ln\left(\frac{e^{2h_i\beta}}{1+e^{2h_i\beta}}\right) + \left(\frac{1}{e^{2h_i\beta}+1}\right)\ln\left(\frac{1}{1+e^{2h_i\beta}}\right)$$

$$= \frac{-(1+e^{2\beta h_i})\ln(1+e^{2h_i\beta}) + e^{2\beta h_i}\ln(e^{2\beta h_i})}{1+e^{2\beta h_i}}$$

$$= -\ln(1+e^{2h_i\beta}) + \frac{\ln(e^{2\beta h_i})}{e^{-2\beta h_i}+1}$$

$$-\sum_i^N h_i m_i = -\sum_i^N h_i\left(\frac{e^{2h_i\beta}-1}{e^{2h_i\beta}+1}\right)\cdot\frac{e^{-2h_i\beta}}{e^{-2h_i\beta}}$$

$$G = \sum_i^N -kT\ln(1+e^{2h_i\beta}) + \frac{1}{e^{-2\beta h_i}+1}\left[kT\ln(e^{2\beta h_i}) + h_i\left(e^{-2h_i\beta}-1\right)\right]$$

$$\boxed{G_{min} = -kT\sum_i \ln\left(e^{\beta h_i} + e^{-\beta h_i}\right)}$$

Do we need to simplify?

4

For the 1-dimensional Ising model with periodic boundary condition, the Hamiltonian is given by

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Use the transfer matrix method to obtain an exact solution in the limit of large N. In particular,

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$$Z = \mathrm{Tr}(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N \approx \lambda_+^N \tag{4}$$

with the transfer matrix

$$\mathbf{T} = \begin{pmatrix} e^{\beta K + \beta h} & e^{-\beta K} \\ e^{-\beta K} & e^{\beta K - \beta h} \end{pmatrix} \tag{5}$$

and λ_+ the larger of the two eigenvalues of the transfer matrix, λ_+ and λ_-.

lecture 14 notes

i) $H = -K \sum_i s_i s_{i+1} - h \sum_i^N s_i$

$$Z = \sum_{s_1 = \pm 1} \cdots \sum_{s_N = \pm 1} \left[e^{K\beta s_1 s_2 + \frac{1}{2} h\beta (s_1 + s_2)}\right]\left[e^{K\beta s_2 s_3 + \frac{1}{2} h\beta (s_2 + s_3)}\right] \cdots \left[e^{K\beta s_N s_1 + \frac{1}{2} h\beta (s_N + s_1)}\right]$$

transfer matrix

$$T = \begin{pmatrix} e^{\beta K + \beta h} & e^{-\beta K} \\ e^{-\beta K} & e^{\beta K - \beta h} \end{pmatrix}$$

Dirac Notation $\rightarrow$ orthonormal bias

$$\sum_{s=\pm 1} |s\rangle\langle s| = I, \quad |s\rangle, \langle s| = (|s\rangle^T)$$

terms in sum become

$$e^{K\beta s_i s_{i+1} + \frac{1}{2}\beta h (s_i + s_{i+1})} = \langle s_i | T | s_{i+1} \rangle$$

$$Z = \sum_{s_1 = \pm 1} \cdots \sum_{s_N = \pm 1} \langle s_1 | T | s_2 \rangle \langle s_2 | T | s_3 \rangle \cdots \langle s_N | T | s_1 \rangle$$

$$= \sum_{S_1 = \pm 1} \langle S_1 | T^N | S_1 \rangle = \mathrm{Tr}(T^N)$$

- diagonalize T w/ U (unitary rotational matrix)

$$T_D = U^{-1} T U$$

$$\hookrightarrow T = U T_D U^{-1}$$

$$Z = \mathrm{Tr}(T^N) = \mathrm{Tr}(U T_D^N U^{-1}) = \mathrm{Tr}(T_D^N)$$

$$\hookrightarrow \mathrm{Tr}(ABC) = \mathrm{Tr}(BCA) = \mathrm{Tr}(CAB)$$

- now write T_D in terms of its eigenvalues

$$T_D = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \leftarrow \det|T - \lambda I| = 0$$

$$\boxed{Z = \lambda_+^N + \lambda_-^N \approx \lambda_+^N} \quad (\text{as } N \to \infty)$$

ii) *(10 points)* Show that the eigenvalues are

$$\lambda_\pm = \mathrm{e}^{\beta K}\cosh(\beta h) \pm \sqrt{\mathrm{e}^{2\beta K}\sinh^2(\beta h) + \mathrm{e}^{-2\beta K}}$$

$$\det|T - \lambda I| = 0 = \det\begin{bmatrix} e^{\beta K + \beta h} - \lambda & e^{-\beta K} \\ e^{-\beta K} & e^{\beta K - \beta h} - \lambda \end{bmatrix}$$

$$(e^{\beta K - \beta h} - \lambda)(e^{\beta K + \beta h} - \lambda) - e^{-2\beta K} = 0$$

$$e^{\beta K-\beta h} e^{\beta K+\beta h} - \lambda e^{\beta K-\beta h} - \lambda e^{\beta K+\beta h} + \lambda^2 = e^{-2\beta K}$$

$$e^{2\beta K} - e^{-2\beta K} - \lambda\left(e^{\beta K-\beta h} + e^{\beta K+\beta h}\right) + \lambda^2 = 0$$

$$\lambda_\pm = \frac{\left(e^{\beta K-\beta h} + e^{\beta K+\beta h}\right) \pm \sqrt{\left(e^{\beta K-\beta h} + e^{\beta K+\beta h}\right)^2 - 4\left(e^{2\beta K} - e^{-2\beta K}\right)}}{2}$$

$$\lambda_\pm = e^{\beta K}\cosh(\beta h) \pm \sqrt{\frac{e^{2\beta K}\left(e^{-\beta h} + e^{\beta h}\right)^2}{4} - e^{2\beta K} + e^{-2\beta K}}$$

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

$$\boxed{\lambda_\pm = e^{\beta K}\cosh(\beta h) \pm \sqrt{e^{2\beta K}\sinh^2(\beta h) + e^{-2\beta K}}}$$

iii) *(10 points)* Examine and comment on the behavior of entropy and energy at $T = 0$ and $T = \infty$.

$$F = -kT\ln Z = -kTN\ln\lambda_+$$

$$\langle E \rangle = -\frac{\delta \ln Z}{\delta \beta} = -\frac{\delta \ln(\lambda_+^N + \lambda_-^N)}{\delta \beta}$$

$$S = \frac{1}{T}\left[\langle E \rangle - F\right]$$

$$F = -kT\ln \lambda_+^N + \lambda_-^N$$

$$\frac{e^{\beta h}+e^{-\beta h}-e^{\beta h}+e^{-\beta h}}{2}$$

$$\boxed{\langle E\rangle\big|_{T\to 0} = \langle E\rangle\big|_{\beta\to\infty}}$$

$$\lambda_\pm = e^{\beta K}\cosh(\beta h) \pm \sqrt{e^{2\beta K}\sinh^2(\beta h) + \cancelto{0}{e^{-2\beta K}}}$$

$$= e^{\beta K}\left(\cosh(\beta h) \pm \sinh(\beta h)\right) = \begin{cases} \lambda_+ = e^{\beta K+\beta h} \\ \lambda_- = e^{\beta K-\beta h} \end{cases}$$

$$\ln(\lambda_+^N + \lambda_-^N) = \ln\left(e^{N\beta K}\left(e^{N\beta h} - \cancelto{0}{e^{-N\beta h}}\right)\right) = N\beta(K+h)$$

$$\langle E\rangle = -\frac{\delta N\beta(K+h)}{\delta\beta} \rightsquigarrow \boxed{\langle E\rangle\big|_{T\to 0} = -N(K+h)}$$

$$\boxed{\langle E\rangle\big|_{T\to\infty} = \langle E\rangle\big|_{\beta\to 0}}$$

$$\lambda_\pm = e^{\beta K}\cancelto{1}{\cosh(\beta h)} \pm \sqrt{e^{2\beta K}\cancelto{0}{\sinh^2(\beta h)} + e^{-2\beta K}}$$

$$= \cancelto{1}{e^{\beta K}} \pm \cancelto{1}{e^{-\beta K}} \to \begin{cases} \lambda_+ = 2 \\ \lambda_- = 0 \end{cases}$$

$$\langle E\rangle = -\frac{\delta\ln(2^N)}{\delta\beta} = 0 \rightsquigarrow \boxed{\langle E\rangle\big|_{T\to\infty} = 0}$$

$$S\big|_{T\to 0} = S\big|_{\beta\to\infty}$$

$$F = -\cancel{kT}\left(N\cancel{\beta}(k+n)\right)$$

$$S = \frac{1}{T}\left(\cancelto{0}{-N(k+n) + N(k+n)}\right)$$

$$\boxed{S\big|_{T\to 0} = 0}$$

$$S\big|_{T\to\infty} = S\big|_{\beta\to 0}$$

$$F = -kT\ln\left(2^N + 0\right)$$

$$S = \frac{1}{T}\left(0 + kTN\ln 2\right)$$

$$\boxed{S\big|_{T\to\infty} = kN\ln 2}$$

Bonus on next pg ↓

iv)

(iv) (**Bonus 15 points**) Show that the spin-spin correlation function at zero external field is given by

$$\langle s_i s_{i+r}\rangle = \frac{\lambda_+^{N-r}\lambda_-^{r} + \lambda_-^{N-r}\lambda_+^{r}}{\lambda_+^{N}+\lambda_-^{N}} \approx \left(\frac{\lambda_-}{\lambda_+}\right)^{r} \equiv \mathrm{e}^{-r/\xi} \tag{7}$$

with the correlation length

$$\xi = \left[\ln\left(\frac{\lambda_+}{\lambda_-}\right)\right]^{-1} = -\frac{1}{\ln\tanh(\beta K)} \tag{8}$$

For Problem 4, you may consult any reference materials, including books and online resources. However, the work you write down must reflect your own understanding.

$$\langle S_i S_{i+r}\rangle = \frac{1}{Z}\,\mathrm{Tr}\left[S_i S_{i+r}\, \underbrace{e^{-\beta H}}_{1 \text{ for } H=0}\right]$$

spin correlation fxn

$$\mathrm{Tr}\left[S_i S_{i+r} e^{-\beta H}\right] = \mathrm{Tr}\left[T(S_1,S_2)\,T(S_2,S_3)\cdots T(S_N,S_1)\right]$$

$$= \mathrm{Tr}\left[T^{i-1} S_z T^{i+r-1} S_z T^{N-i-r+1}\right]$$

$$= \mathrm{Tr}\left[T^{N-r} S_z T^{r} S_z\right]$$

diagonalize

$$= \mathrm{Tr}\left[(UTU^{-1})^{N-r}(US_zU^{-1})(UTU^{-1})^{r}(US_zU^{-1})\right]$$

$$U = \begin{pmatrix} \cos\theta/2 & -\sin\theta/2 \\ \sin\theta/2 & \cos\theta/2 \end{pmatrix}, \quad U^{-1} = \begin{pmatrix} \cos\frac{\theta}{2} & \sin\theta/2 \\ -\sin\theta/2 & \cos\theta/2 \end{pmatrix}$$

$$S_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \longrightarrow (US_zU^{-1}) = \begin{bmatrix} \cos\theta & -\sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$= \mathrm{Tr}\left[\begin{bmatrix} \lambda_+^{N-r} & 0 \\ 0 & \lambda_-^{N-r} \end{bmatrix}\begin{bmatrix} \cos\theta & -\sin\theta \\ -\sin\theta & -\cos\theta \end{bmatrix}\begin{bmatrix} \lambda_+^{r} & 0 \\ 0 & \lambda_-^{r} \end{bmatrix}\begin{bmatrix} \cos\theta & -\sin\theta \\ -\sin\theta & -\cos\theta \end{bmatrix}\right]$$

• 2 rotations give inverse and I

$$= \mathrm{Tr}\left[\begin{bmatrix} \lambda_+^{N-r} & 0 \\ 0 & \lambda_-^{N-r} \end{bmatrix}\begin{bmatrix} \lambda_+^{r} & 0 \\ 0 & \lambda_-^{r} \end{bmatrix}^{-1}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\right]$$

$$= \mathrm{Tr}\begin{bmatrix} \lambda_+^{N-r}\lambda_-^{r} & 0 \\ 0 & \lambda_-^{N-r}\lambda_+^{r} \end{bmatrix}$$

$$\langle S_i S_{i+r}\rangle = \frac{\lambda_+^{N-r}\lambda_-^{r} + \lambda_-^{N-r}\lambda_+^{r}}{\lambda_+^{N} + \lambda_-^{N}} =$$

$$= \frac{\left(\frac{\lambda_+}{\lambda_-}\right)^{N-r} + \cancel{\left(\frac{\lambda_+}{\lambda_-}\right)^{r}}}{\left(\frac{\lambda_+}{\lambda_-}\right)^{N} + \cancel{1}} \approx \left(\frac{\lambda_+}{\lambda_-}\right)^{-r} \approx \left(\frac{\lambda_-}{\lambda_+}\right)^{r}$$

$N >> r$

for $H = 0$ (no field)

$$\left(\frac{\lambda_-}{\lambda_+}\right)^{r} = \left[\frac{e^{\beta K}\xrightarrow{1}{\cancel{\cosh(\beta h)}} - \sqrt{e^{2\beta K}\xrightarrow{0}{\cancel{\sinh^2(\beta h)}} + e^{-2\beta K}}}{e^{\beta K}\xrightarrow{1}{\cancel{\cosh(\beta h)}} + \sqrt{e^{2\beta K}\xrightarrow{0}{\cancel{\sinh^2(\beta h)}} + e^{-2\beta K}}}\right]^{r}$$

$$= \left[\frac{e^{\beta K} - e^{-\beta K}}{e^{\beta K} + e^{-\beta K}}\right]^{r} = [\tanh(\beta K)]^{r}$$

$$\xi^{-1}_{e} = \left[\ln_e\left[\frac{\lambda_+}{\lambda_-}\right]\right]^{-1} = -\left[\ln_e(\tanh(\beta K))\right]^{-1}$$

$$\boxed{\langle S_i S_{i+r}\rangle \approx \left(\frac{\lambda_-}{\lambda_+}\right)^{r} \equiv e^{-r/\xi}}$$

https://bingweb.binghamton.edu/~suzuki/ThermoStatFIles/16.9%20PT%201D%20%20Ising%20model.pdf