Zahra Shirji

Ch/ChE 164 Winter 2024
Homework Problem Set #7
Due Date: Thursday, March 7, 2024 @ 11:59pm PT
Out of 100 Points
Project - Work on Questions 1 and 2

1. The Gibbs-Bogoliubov-Feynmann (GBF) variational principle can be used to approximately evaluate integrals. Consider the following integral, which does not admit of an analytical closed form expression:

$$I = \int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}ax^2 - \frac{1}{4!}ux^4\right) \tag{1}$$

where a and u are positive constants. We can regard the exponent as a "Hamiltonian"

$$H = \frac{1}{2}ax^2 + \frac{1}{4!}ux^4 \tag{2}$$

Use the GBF variational method to evaluate the integral approximately by making a reference "Hamiltonian"

$$H_R = \frac{1}{2}Ax^2 \tag{3}$$

(i) *(10 points)* Derive an expression for A in terms of the parameters a and u;

(ii) *(5 points)* Obtain an approximate expression for the integral I;

(iii) *(5 points)* Make a plot of the approximate expression and compare it with the numerical value of the integral for some parameter selections.

(iv) *(5 points)* Based on your results from (iii) and (iv), comment on the effects of a and u on the accuracy of the GBF method.

2. Simple liquid crystals are systems consisting of anisotropic, e.g., rod-like molecules. At high temperatures, the orientations of these molecules are random; this is called the isotropic phase. At low temperatures, molecules align parallel to each other; this is called the nematic phase. The simplest lattice model for this transition is a 3-state model in which a molecule can take any one of the three (x, y, z) orthogonal orientations. If two nearest neighbor molecules lie parallel to each other, there is an energy gain of $-\varepsilon < 0$. Otherwise there is no gain. Assuming single occupancy on each site and no vacancy, we may define variables $\sigma_x(i), \sigma_y(i), \sigma_z(i)$, such that $\sigma_x(i) = 1$ if molecule i lies parallel to the x-axis and $\sigma_x(i) = 0$ if not, and likewise for other directions. (Of course, $\sigma_x(i) + \sigma_y(i) + \sigma_z(i) = 1$.)

The average $\langle\sigma_\alpha(i)\rangle (\alpha = x, y, z)$ gives the fraction of molecules oriented along the α-axis. If we take the z-axis as the orientation in the nematic state, we may define an order parameter as

$$S = \frac{1}{2}(3\langle\sigma_z\rangle - 1) \tag{4}$$

such that in the isotropic state $S = 0$ and in the nematic state $S > 0$.

(i) *(15 points)* Construct a mean field free energy (per molecule) in terms of the order parameter S.

(ii) *(10 points)* Expand the free energy to 4th order in S. From the form of this free energy, can you tell whether the isotropic-nematic transition is first or second order?

(ii) *(15 points)* Use the approximate free energy in (ii) to find the isotropic-nematic transition temperature, the value of the order parameter for both phases at the transition, and the latent heat of the transition (the difference of energy between two states.)

3. Consider the lattice gas model with a grand partition function

$$\Xi(\mu, V, T) = \sum_{\{\sigma_i\}} exp \left\{ \beta\mu \sum_i \sigma_i + \beta\varepsilon_0 \sum_{\langle ij \rangle} \sigma_i \sigma_j \right\} \tag{5}$$

(i) *(15 points)* Show that there exists a one-to-one correspondence between the parameters in the lattice gas model with those in the Ising model. In particular, show that the pressure for the lattice gas, p, is related to the free energy per spin of the Ising model, f, via

$$p = -\frac{1}{2} zJ + h - f. \tag{6}$$

(We have taken the volume of a lattice site to be 1.)

(i) *(20 points)* Use the random mixing approximation to derive the pressure-density equation of state for the lattice gas (without using the above correspondence).

1

1. The Gibbs-Bogoliubov-Feynmann (GBF) variational principle can be used to approximately evaluate integrals. Consider the following integral, which does not admit of an analytical closed form expression:

$$I = \int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}ax^2 - \frac{1}{4!}ux^4\right) \tag{1}$$

where a and u are positive constants. We can regard the exponent as a "Hamiltonian"

$$H = \frac{1}{2}ax^2 + \frac{1}{4!}ux^4 \tag{2}$$

Use the GBF variational method to evaluate the integral approximately by making a reference "Hamiltonian"

$$H_R = \frac{1}{2}Ax^2 \tag{3}$$

(i) *(10 points)* Derive an expression for A in terms of the parameters a and u;

$$f = -\ln I \leq f_R + \langle H \rangle_R - \langle H_R \rangle_R$$

· take expectations wrt. reference

$$\langle H_R \rangle_R = \cancel{\left(\frac{A}{2\pi}\right)^{1/2}} \underbrace{\int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{2}Ax^2\right)}_{\cancel{(2\pi/A)^{1/2}} \left(\frac{\cancel{2}}{\cancel{2}\cancel{A}}\right)\left(\frac{1}{2}\cancel{A}\right)}$$

gaussian integral

$$\int_{-\infty}^{\infty} x^2 e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$$

$$\left[\langle H_R \rangle_R = \frac{1}{2}\right.$$

gaussian again

$$f_R = -\ln \int_{-\infty}^{\infty} e^{-\frac{1}{2}Ax^2} = -\ln\left(\sqrt{\frac{2\pi}{A}}\right) \rightarrow \left[f_R = \frac{1}{2}\ln\frac{A}{2\pi}\right.$$

$$\langle H \rangle_R = \left(\frac{A}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx \cdot \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{2}ax^2, \frac{1}{4!}ux^4\right)$$

used mathematica → see below

$$\left[\langle H \rangle_R = \frac{4aA + u}{8A^2}\right.$$

$$f = -\ln I \leq \frac{1}{2}\ln\frac{A}{2\pi} + \frac{4aA+u}{8A^2} - \frac{1}{2} \equiv f_{var}$$

- minimize f_{var} wrt A

$$\frac{\delta f_{var}}{\delta A} = \frac{1}{2}\cdot\frac{1}{A} + \frac{a}{2A^2} - \frac{4aA+u}{4A^3} = 0 \quad \times 4A^3$$

- solve for A $\quad 2A^2 - 2aA - u = 0$

$$\boxed{A = \frac{2a + \sqrt{4a^2+8u}}{4}}$$

only keep positive root

ii) (ii) *(5 points)* Obtain an approximate expression for the integral I;

$$e^{-\ln I} \leq e^{f_R} + e^{\langle H \rangle_R} - e^{\langle H_R \rangle_R}$$

$$f_R = -\ln I \rightarrow I = \sqrt{\frac{2\pi}{A}}$$

$$\boxed{I = \sqrt{\frac{2\pi}{A}}\exp\left[-\frac{4aA+u}{8A^2} + \frac{1}{2}\right]}$$

iii) (iii) *(5 points)* Make a plot of the approximate expression and compare it with the numerical value of the integral for some parameter selections.

$$I = \int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}ax^2 - \frac{1}{4!}ux^4\right) = \int_{-\infty}^{\infty} dx\, e^{-\left(\frac{1}{4!}u(x^2)^2 + \frac{1}{2}a(x^2)\right)}$$

$$\int_{-\infty}^{\infty} dx\, e^{-(ax^2+bx+c)} \approx \sqrt{\frac{\pi}{a}}\, e^{b^2/4a - c}$$

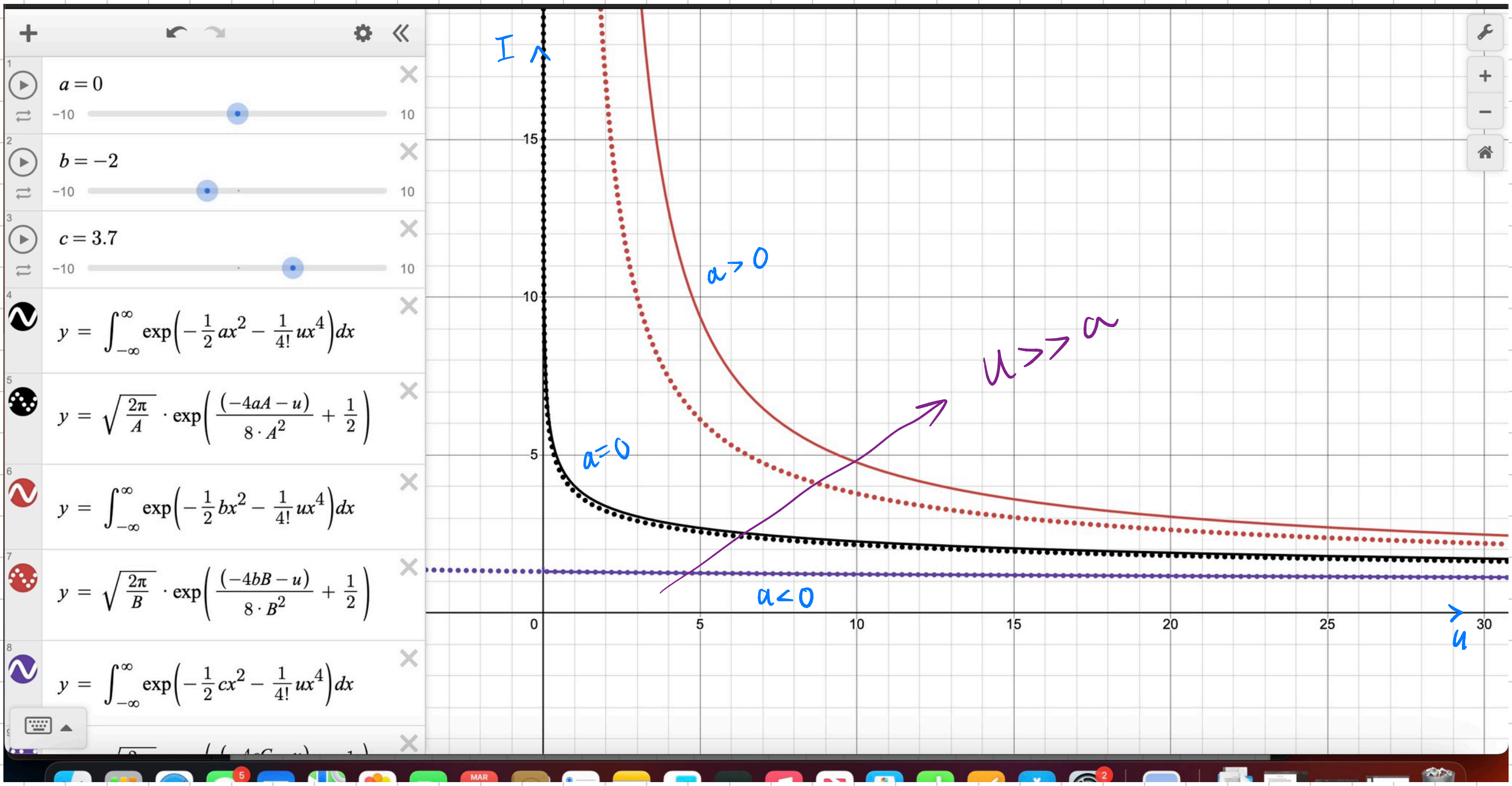
gaussian

$$I \approx \sqrt{\frac{24\pi}{u}}\, e^{\frac{1}{4}a^2 24/4\cdot u}$$

$$\boxed{I \approx \sqrt{\frac{24\pi}{u}}\, e^{3a^2/2u}}$$

numeric value

Plotted on desmos



· the approximate integral fails as a valid approximation a u grows relative to a (u >> a)

WOLFRAM MATHEMATICA *Plan:* California Institute of Technology

StatMech_HW7_1a.nb

```
In[12]:= H = 1/2*a*x^2+1/(4!)*u*x^4
         Hr = 1/2*A*x^2
         avg_H = Assuming[{Re[a] ≥ 0, Re[A] ≥ 0, Re[u] ≥ 0}, (A/(2*Pi))^(1/2)*Integrate[H*Exp[-Hr], {x, -Infinity, Infinity}]]
```

Out[12]= $\frac{a x^2}{2} + \frac{u x^4}{24}$

Out[13]= $\frac{A x^2}{2}$

Set : Tag Plus in avg : Blank$\left[\frac{a x^2}{2} + \frac{u x^4}{24}\right]$ is Protected.

Out[14]= $\frac{4 a A + u}{8 A^2}$ if $Re[A] > 0$

(2)

2. Simple liquid crystals are systems consisting of anisotropic, e.g., rod-like molecules. At high temperatures, the orientations of these molecules are random; this is called the isotropic phase. At low temperatures, molecules align parallel to each other; this is called the nematic phase. The simplest lattice model for this transition is a 3-state model in which a molecule can take any one of the three (x, y, z) orthogonal orientations. If two nearest neighbor molecules lie parallel to each other, there is an energy gain of $-\varepsilon < 0$. Otherwise there is no gain. Assuming single occupancy on each site and no vacancy, we may define variables $\sigma_x(i), \sigma_y(i), \sigma_z(i)$, such that $\sigma_x(i) = 1$ if molecule i lies parallel to the x-axis and $\sigma_x(i) = 0$ if not, and likewise for other directions. (Of course, $\sigma_x(i) + \sigma_y(i) + \sigma_z(i) = 1$.)

The average $\langle \sigma_\alpha(i) \rangle (\alpha = x, y, z)$ gives the fraction of molecules oriented along the α-axis. If we take the z-axis as the orientation in the nematic state, we may define an order parameter as

$$S = \frac{1}{2}(3\langle \sigma_z \rangle - 1) \tag{4}$$

such that in the isotropic state $S = 0$ and in the nematic state $S > 0$.

(i) *(15 points)* Construct a mean field free energy (per molecule) in terms of the order parameter S.

i) $F = E - TS = \langle H \rangle - TS$

$S = -k \sum P \ln P$

$P_\alpha = \langle \sigma_\alpha \rangle$

$S = \frac{1}{2}(3\langle \sigma_z \rangle - 1)$

solve for $\langle \sigma_z \rangle$

$\langle \sigma_z \rangle = \frac{2S+1}{3}$

$\langle \sigma_x \rangle = \langle \sigma_y \rangle$

$2\langle \sigma_x \rangle + \langle \sigma_z \rangle = 1$ (all prob sum to 1)

$\langle \sigma_x \rangle = \langle \sigma_y \rangle = \frac{1-S}{3}$

$$S = -k \sum_i^N \left(\frac{2(1-S)}{3} \ln \frac{1-S}{3} + \frac{2S+1}{3} \ln \frac{2S+1}{3} \right)$$

$$S = -kN \left(\frac{2(1-S)}{3} \ln \frac{1-S}{3} + \frac{2S+1}{3} \ln \frac{2S+1}{3} \right)$$

$\langle H \rangle = \sum_{i,j,\alpha} -\varepsilon \sigma_{i,\alpha} \sigma_{j,\alpha}$ $\longrightarrow$ sum over N sites w/ coordination z

$= \frac{Nz}{2} \left(-\varepsilon \left(\langle \sigma_x \rangle^2 + \langle \sigma_y \rangle^2 + \langle \sigma_z \rangle^2 \right) \right)$ $\div 2$ to avoid double count

$$= -\varepsilon \frac{Nz}{2}\left(2\left(\frac{1-S}{3}\right)^2 + \left(\frac{2S+1}{3}\right)^2\right)$$

$$\frac{2 - \cancel{4S} + 2S^2}{9} + \frac{4S^2 \cancel{+4S} + 1}{9} \rightarrow \frac{6S^2+3}{9}$$

$$\langle H \rangle = -\varepsilon N z\left(\frac{2S^2+1}{6}\right)$$

$$\boxed{F = -\varepsilon N z\left(\frac{2S^2+1}{6}\right) + TNk\left(\frac{2(1-S)}{3}\ln\frac{1-S}{3} + \frac{2S+1}{3}\ln\frac{2S+1}{3}\right)}$$

ii) *(10 points)* Expand the free energy to 4th order in S. From the form of this free energy, can you tell whether the isotropic-nematic transition is first or second order?

T.E. ln terms around $S=0$

$$\ln\left(\frac{1-S}{3}\right) = -\ln(3) - S - \frac{S^2}{2} - \frac{S^3}{3} - \frac{S^4}{4} + \dots$$

$$\ln\left(\frac{2S+1}{3}\right) = -\ln(3) + 2S - 2S^2 + \frac{8}{3}S^3 - 4S^4 + \dots$$

plug into F:

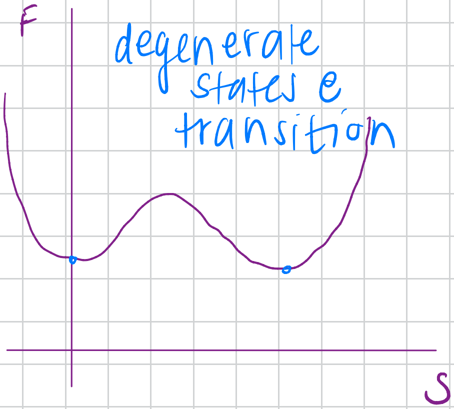
$$F = -\varepsilon N z\left(\frac{2S^2+1}{6}\right) + TNk\Big[\frac{2}{3}\Big(-\cancel{\ln(3)} - \cancel{S} - \cancel{\frac{S^2}{2}} - \cancel{\frac{S^3}{3}} - \cancel{\frac{S^4}{4}} + \cancel{S\ln 3} + \cancel{S^2}$$

$$+ \cancel{\frac{S^3}{2}} + \cancel{\frac{S^4}{3}} + \dots\Big) + \frac{1}{3}\Big(-\cancel{2S\ln(3)} + \cancel{4S^2} - \cancel{4S^3} + \cancel{\frac{32}{3}}S^4 - \cancel{\ln(3)} + \cancel{2}S - \cancel{2S^2} + \cancel{\frac{8}{3}S^3} - \cancel{4S^2} + \dots\Big)\Big]$$

$$\boxed{F = -\varepsilon N z\left(\frac{2S^2+1}{6}\right) + TNk\left[-\ln 3 + S^2 - \frac{1}{3}S^3 + \frac{1}{2}S^4\right]}$$

[first order transition] b/c no S^1 term

iii) *(15 points)* Use the approximate free energy in (ii) to find the isotropic-nematic transition temperature, the value of the order parameter for both phases at the transition, and the latent heat of the transition (the difference of energy between two states.)



first-order transition

$$\frac{\delta F}{\delta S}(0,T^*) = \frac{\delta F}{\delta S}(S^*,T^*)$$

$$F(0,T^*) = F(S^*,T^*)$$

$$\frac{\delta F}{\delta S} = 0 = -\epsilon N z\left(\frac{4S}{6}\right) + NkT\left(2S - S^2 + 2S^3\right) \qquad (1)$$

$F(0) = F(S^*) \longrightarrow$ below

$$-\frac{\epsilon z N}{6} - T^* N k \ln(3) = -\frac{\epsilon z N}{6}\left(2S^{*2}+1\right) + NkT^*\left[S^{*2} - \tfrac{1}{3}S^{*3} + \tfrac{1}{2}S^{*4} - \ln(3)\right] \qquad (2)$$

find intersection on desmos
- get $T^* = T^*(S^*)$ (2)
- solve for S^* in (1)

$$\boxed{T^* = \frac{6\epsilon z}{17k}}$$

$$\boxed{S^* = 1/3} \xrightarrow[\text{order param}]{\text{plug into}} \boxed{\langle \sigma_z \rangle = 5/9}$$

latent heat: ordered - disorder

$$\langle H \rangle = \frac{-\epsilon z N}{6}\left(2S^2+1\right)$$

$$H = \langle H(S=0)\rangle - \langle H(S=S^*)\rangle = \boxed{-\frac{N\epsilon z}{27} = H^*}$$

$$j \cdot N \cdot z\left(\frac{4x}{6}\right) = N \cdot k \cdot y \cdot \left(2x - x^2 + 2x^3\right)$$

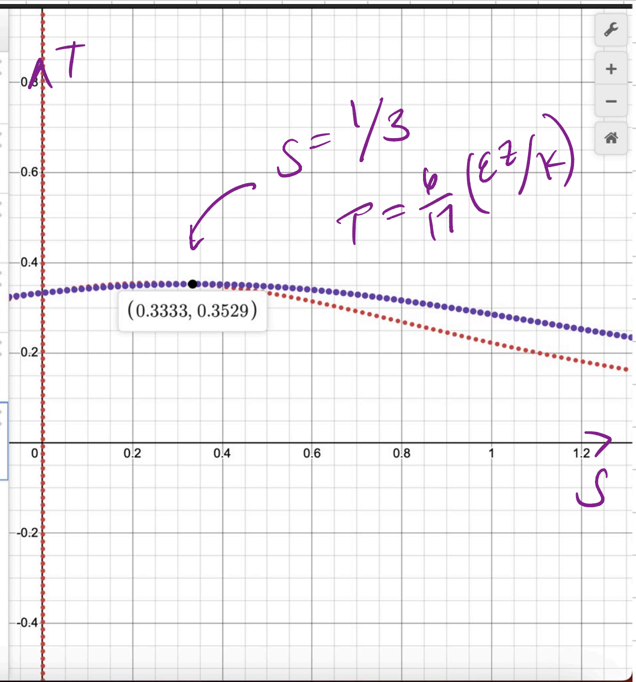
$N = 1$

$z = 1$

$k = 1$

$j = 1$

$$-j \cdot N \cdot \frac{z}{6} - N \cdot k \cdot y \cdot \ln(3) = -j \cdot N \cdot \frac{z}{6}\left(2x^2 + 1\right) + Nky\left(x^2 - \frac{x^3}{3} + \frac{1}{2}x^4 - \ln(3)\right)$$



3 . Consider the lattice gas model with a grand partition function

$$\Xi(\mu, V, T) = \sum_{\{\sigma_i\}} exp\left\{\beta\mu\sum_i \sigma_i + \beta\varepsilon_0 \sum_{\langle ij\rangle} \sigma_i\sigma_j\right\} \tag{5}$$

(i) *(15 points)* Show that there exists a one-to-one correspondence between the parameters in the lattice gas model with those in the Ising model. In particular, show that the pressure for the lattice gas, p, is related to the free energy per spin of the Ising model, f, via

$$p = -\frac{1}{2}zJ + h - f. \tag{6}$$

(We have taken the volume of a lattice site to be 1.)

i) from class

$$\sigma_i = \frac{1+s_i}{2}, \quad \sigma_j = \frac{1+s_j}{2}$$

total "volume"

$$\sum_i 1 = M, \quad \sum_{\{ij\}} 1 = \frac{zM}{2}$$

possible interacting pairs, $\frac{1}{2}$ to not overcount

· plug into Ξ

$$\Xi = \sum_{\{s_i\}} \exp\left\{\beta\mu\sum_i \frac{1+s_i}{2} + \beta\varepsilon_0\sum_{\{ij\}}\left(\frac{1+s_i}{2}\right)\left(\frac{1+s_j}{2}\right)\right\}$$

$$= \sum_{\{s_i\}} \exp\left[\beta\mu\frac{1}{2}\left(\sum_i 1 + \sum_i s_i\right) + \beta\varepsilon_0\frac{1}{4}\underbrace{\sum_{\{ij\}}(1+s_i+s_j+s_is_j)}_{\to zM/2}\right]$$

$$= \sum_{\{s_i\}} \exp\left[\beta\mu\frac{M}{2} + \beta\varepsilon_0\frac{zM}{8} + \frac{\beta\mu}{2}\sum_i s_i + \frac{\beta\varepsilon_0}{4}\sum_{\{ij\}} s_is_j + \frac{\beta\varepsilon_0}{4}\sum_{\{ij\}}\underbrace{s_i + s_j}_{z s_i}\right]$$

$$= \sum_{\{s_i\}} \exp\left[\beta\mu\frac{M}{2} + \beta\varepsilon_0\frac{zM}{8} + \left(\frac{\beta\mu}{2} + \frac{\beta\varepsilon_0 z}{4}\right)\sum_i s_i + \frac{\beta\varepsilon_0}{4}\sum_{\{ij\}} s_is_j\right]$$

$$W = -PV = -kT\ln\Xi$$

$$\rightarrow P = \frac{kT}{M}\ln\Xi$$

$$P = \frac{kT}{M}\left[\left(\beta\mu\frac{M}{2} + \beta\varepsilon_0\frac{zM}{8}\right) + \ln\sum_{\{s_i\}}\exp\left[\left(\frac{\beta\mu}{2} + \frac{\beta\varepsilon_0 z}{4}\right)\sum_i s_i + \frac{\beta\varepsilon_0}{4}\sum_{\{ij\}} s_is_j\right]\right]$$

$$P = \frac{\mu}{2} + \frac{\varepsilon_0 z}{8} + \frac{kT}{M} \ln \sum_{\{s_i\}} \exp\left[\left(\underbrace{\frac{\beta\mu}{2} + \frac{\beta\varepsilon_0 z}{4}}_{\beta h}\right)\sum_i s_i + \frac{\beta\varepsilon_0}{4}\sum_{\{ij\}} s_i s_j\right]$$

$$\beta h \rightarrow h = \frac{\mu}{2} + \frac{\varepsilon_0 z}{4}, \quad J = \frac{\varepsilon_0}{4}$$

Ising partition fxn:

$$Z = \sum_{\{s\}} \exp\left[\beta J \sum_i \sum_{i'} s_i s_{i'} + \beta h \sum_i s_i\right]$$

$$= \sum_{\{s_i\}} \exp\left[\beta J \sum_{\{ii'\}} s_i s_{i'} + \beta h \sum_i s_i\right], \quad J = \varepsilon_0/4$$

$$= \sum_{\{s_i\}} \exp\left[\frac{\beta\varepsilon_0}{4} \sum_{\{ii'\}} s_i s_{i'} + \beta h \sum_i s_i\right]$$

$$f = \frac{F}{M} = -\frac{kT \ln Z}{M}$$

$$f = \frac{-kT}{M} \ln \sum_{\{s_i\}} \exp\left[\frac{\beta\varepsilon_0}{4} \sum_{\{ii'\}} s_i s_{i'} + \beta h \sum_i s_i\right]$$

$$P = \frac{\mu}{2} + \frac{\varepsilon_0 z}{8} - f = \underbrace{\left(\frac{\mu}{2} + \frac{\varepsilon_0 z}{4}\right)}_{h} - \underbrace{\frac{\varepsilon_0 z}{8}}_{\frac{J}{2} z} - f$$

$$\boxed{P = -\frac{1}{2} J z + h - f}$$

ii)

(i) *(20 points)* Use the random mixing approximation to derive the pressure-density equation of state for the lattice gas (without using the above correspondence).

· random mixing

$$\langle \sigma_i \rangle = \frac{n}{M} = \sigma_i = \sigma_j = \rho$$

$$\Xi(\mu, V, T) = \sum_{\{\sigma_i\}} exp\left\{\beta\mu \sum_i \sigma_i + \beta\varepsilon_0 \sum_{\langle ij \rangle} \sigma_i \sigma_j\right\}$$

$$\Xi = \sum_{\{\sigma_i\}}^{M} \exp\left(\beta\mu \frac{M}{\cancel{2}} \cancel{2}\rho + \beta \frac{zM}{2} \varepsilon_0 \rho^2\right)$$

$$= \sum_{n=0}^{M} \frac{M!}{(\rho M)!\,(M-\rho M)!} \exp\left(\beta\mu M\rho + \beta \frac{zM}{2} \varepsilon_0 \rho^2\right)$$

we know $\ln \sum \Xi \approx \ln \Xi^*$

· find maximal term Ξ^*,
take deriv of $\ln \Xi$ w.r.t. ρ

$$\frac{\delta}{\delta\rho}\left[\ln \frac{M!}{(\rho M)!\,(M-\rho M)!} \exp\left(\beta\mu M\rho + \beta \frac{zM}{2} \varepsilon_0 \rho^2\right)\right] = 0$$

$$\frac{\delta}{\delta\rho}\Big[M\ln M - \cancel{M} - \rho M \ln \rho M + \cancel{\rho M} - (M-\rho M)\ln(M-\rho M) + \cancel{(M-\rho M)}$$
$$+ \beta\mu M\rho + \beta \frac{zM}{2} \varepsilon_0 \rho^2\Big] = 0$$

simplify in terms

$$\cancel{M \ln M} - \rho^* M \ln \rho^* - \cancel{\rho^* M \ln M} - \cancel{M \ln M} - M\ln(1-\rho^*) + \cancel{\rho^* M \ln M} + \rho^* M \ln(1-\rho^*)$$

$$= \rho^* M \ln\left(\frac{1-\rho^*}{\rho^*}\right)$$

$$\beta\mu + \beta z \varepsilon_0 \rho^* + \rho^* \ln\left(\frac{1-\rho^*}{\rho^*}\right) = 0$$

$$\left\{ \beta\mu + \beta z \varepsilon_0 \rho^* = \ln\left(\frac{\rho^*}{1-\rho^*}\right) \right.$$

· cannot solve, assume $\rho = \rho^*$

$$W = -PM = -kT \ln \Xi \longrightarrow P = \frac{kT}{M} \ln \Xi$$

$$\Xi = \Xi^* \longrightarrow P = \frac{kT}{M} \ln \Xi^*$$

$$P = \frac{kT}{M}\left[\rho^* M \ln\left(\frac{\rho^*}{1-\rho^*}\right) - \ln(1-\rho^*) + \beta\mu M \rho^* + \beta z \frac{M}{2} \varepsilon_0 \rho^{*2}\right]$$

$$= -\rho^*(\cancel{\mu} + z\varepsilon_0\rho^*) - kT \cdot \ln(1-\rho^*) + \cancel{\mu\rho^*} + \frac{z}{2}\varepsilon_0 \rho^{*2}$$

$$\boxed{P = -kT \cdot \ln(1-\rho^*) - \frac{z}{2}\varepsilon_0 \rho^{*2}}$$