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

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"

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

1.1

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

To start with, we can consider the inequality $I \leq I_R \exp\left(\langle H - H_R \rangle_R\right)$, where I_R is the reference integral for the initial integral I, and $\langle H - H_R \rangle_R$ is the expectation value of the difference between the Hamiltonian and the reference Hamiltonian, evaluated at the reference probability. Our first task is to evaluate the reference integral:

$$I_R = \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right) dx = \sqrt{\frac{2\pi}{A}} \tag{1}$$

We cognize this also as a reference partition function. Next, we want to find the reference free energy, and it is given by:

$$F_R = -\ln I_R = -\ln \sqrt{\frac{2\pi}{A}} = -\frac{1}{2}\ln\frac{2\pi}{A} \tag{2}$$

Next, we want to compute $\langle H - H_R \rangle_R$, and it is given by:

$$\langle H - H_R \rangle_R = \frac{1}{I_R}\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{2}ax^2 + \frac{1}{4!}ux^4 - \frac{1}{2}Ax^2\right) dx \tag{3}$$

We can plug in the expression that we found for the I_R and also combine the ex squared terms in the second prentices of the grand: we can make the integrand into 2 integrals by distribution:

$$\langle H - H_R \rangle_R = \frac{1}{\sqrt{\frac{2\pi}{A}}}\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\left(\frac{1}{2}a - \frac{1}{2}A\right)x^2 + \frac{1}{4!}ux^4\right) dx \tag{4}$$

$$\langle H - H_R \rangle_R = \frac{1}{\sqrt{\frac{2\pi}{A}}}\left(\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\left(\frac{1}{2}a - \frac{1}{2}A\right)x^2\right) dx + \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{4!}ux^4\right) dx\right) \tag{5}$$

For the first integral, we have:

$$\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\left(\frac{1}{2}a - \frac{1}{2}A\right)x^2\right) dx = \sqrt{\frac{2\pi}{A}} \cdot \frac{1}{A^2}\left(\frac{1}{2}a - \frac{1}{2}A\right) \tag{6}$$

For the second integral, we have:

$$\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{4!}ux^4\right)dx = \frac{3u\sqrt{2\pi}}{A^{5/2}} \tag{7}$$

So, we can plug in the results of the integrals into the expression for $\langle H - H_R \rangle_R$ and we divide by a factor of $\sqrt{\frac{2\pi}{A}}$ to get:

$$\langle H - H_R \rangle_R = \frac{1}{A^2}\left(\frac{1}{2}a - \frac{1}{2}A\right) + \frac{3u}{A^{5/2}} \tag{8}$$

The GBF inequaliy tells us that we can find the variational parameter by minimizing the sum of F_R and $\langle H - H_R \rangle_R$ with respect to A:

$$\frac{\partial}{\partial A}\left(F_R + \langle H - H_R \rangle_R\right) = 0 \tag{9}$$

Plugging in the expressions for F_R and $\langle H - H_R \rangle_R$, we get:

$$\frac{\partial}{\partial A}\left(-\frac{1}{2}\ln\frac{2\pi}{A} + \frac{1}{A^2}\left(\frac{1}{2}a - \frac{1}{2}A\right) + \frac{3u}{A^{3/2}}\right) = 0 \tag{10}$$

The derivative of the first term is:

$$\frac{\partial}{\partial A}\left(-\frac{1}{2}\ln\frac{2\pi}{A}\right) = \frac{1}{2A} \tag{11}$$

The derivative of the second term is:

$$\frac{\partial}{\partial A}\left(\frac{1}{A^2}\left(\frac{1}{2}a - \frac{1}{2}A\right)\right) = \frac{\partial}{\partial A}\left(\frac{a}{2A^3} - \frac{1}{2A^2}\right) = \frac{-3a}{2A^4} + \frac{1}{A^3} \tag{12}$$

The derivative of the third term is:

$$\frac{\partial}{\partial A}\left(\frac{3u}{A^{3/2}}\right) = \frac{-9u}{2A^{5/2}} \tag{13}$$

Combining the derivatives, we get:

$$\frac{1}{2A} + \frac{-3a}{2A^4} + \frac{1}{A^3} + \frac{-9u}{2A^{5/2}} = 0 \tag{14}$$

Multiplying through by A^4 to clear the denominators, we get:

$$\frac{A^3}{2} - \frac{3a}{2} + A - \frac{9uA^{3/2}}{2} = 0 \tag{15}$$

I do not get a result here and not sure why.

1.2

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

1.3

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

1.4

(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

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

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

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

2.1 (

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

2.2 (

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

2.3 (

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

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).