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

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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 $I = I_R \langle \exp[-(H - H_R)] \rangle_R \geq I_R \exp[-\langle H \rangle_R + \langle H_R \rangle_R]$. We can use the reference Hamiltonian to compute the reference partition function, which is given by:

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

We cognize this also as a reference partition function. Now come we want to compute the quantities $\langle H \rangle_R$ and $\langle H_R \rangle_R$. We can substitute our expression for I_R into the expression for $\langle H \rangle_R$ to get:

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

We can make the integrand into 2 integrals by distribution:

$$\langle H \rangle_R = \sqrt{\frac{A}{2\pi}} \left(\int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{2}ax^2\right) dx + \int_{-\infty}^{\infty} \exp\left(-\frac{1}{2}Ax^2\right)\left(\frac{1}{4!}ux^4\right) dx \right) = \frac{a}{2A} + \frac{u}{8A^2} \tag{3}$$

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

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

And then we want to find the value of A that maximizes the quantity $I_R \exp[-\langle H \rangle_R + \langle H_R \rangle_R]$.

$$\frac{\partial}{\partial A}\left(I_R \exp[-\langle H \rangle_R + \langle H_R \rangle_R]\right) \tag{5}$$

Minimizing this expression is equivalent to maximizing is logarithm:

$$\frac{\partial}{\partial A}\left(\ln I_R - \langle H \rangle_R + \langle H_R \rangle_R\right) = 0 \tag{6}$$

This gives us:

$$2A^2 - 2aA - u = 0 \tag{7}$$

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We can solve for A to get:

$$A = \frac{a \pm \sqrt{a^2 + 2u}}{2} \tag{8}$$

from which we only keep the positive root:

$$A = \frac{a + \sqrt{a^2 + 2u}}{2} \tag{9}$$

1.2

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

The maximum value for this expression is going to be bounded by:

$$I \leq I_R \exp[-\langle H \rangle_R + \langle H_R \rangle_R] = \sqrt{\frac{2\pi}{A}} \exp\left[-\frac{a}{2A} - \frac{u}{8A^2} + \frac{1}{2}\right] \tag{10}$$

with all of these quantities as defined above.

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.

```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.integrate import quad, IntegrationWarning

# Define the range for u
u_range = np.linspace(0.0, 10, 100)

# Parameters a for each condition
a_values = [-0.5, 0, 0.5]

# Define the actual integrand with safe checks
def exact(x, a, u):
    return np.exp(-0.5 * a * x**2 - (u/24) * x**4)

```
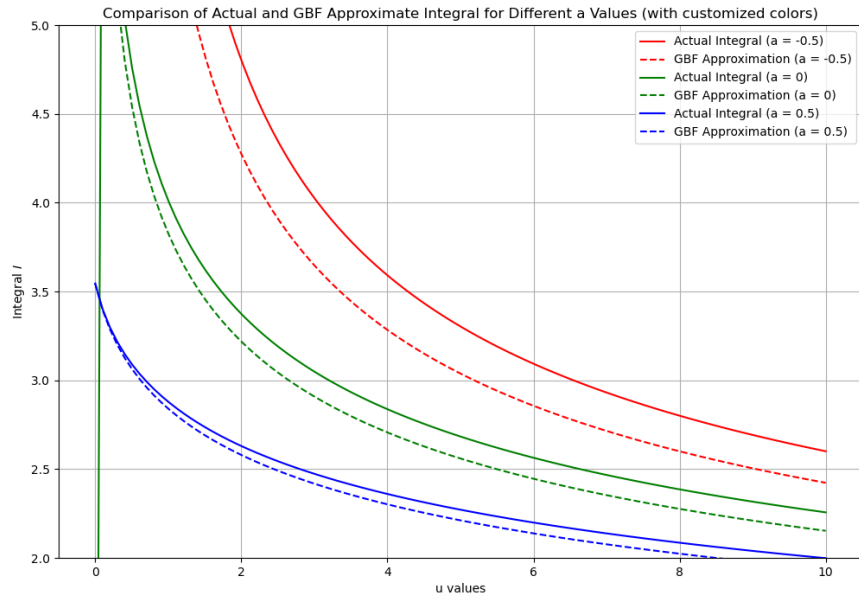
Figure 1: Comparison of Actual and GBF Approximate Integral for Different a Values (with customized colors)

```
15 # Define the GBF approximate integral
16 def approximant(a, u):
17     A = (a + np.sqrt(a**2 + 2*u)) / 2
18     approx = np.sqrt(2 * np.pi / A) * np.exp(-a / (2*A) - u /
        (8*A**2) + 1/2)
19     return approx
20
21 # Containers for numerical and GBF approximate results, with
      checks for safe computation
22 exact_results = {a_val: [] for a_val in a_values}
23 approx_results = {a_val: [] for a_val in a_values}
24
25 # Calculate the numerical and GBF approximate integrals for
      each a and range of u
26 for a_val in a_values:
27     for u_val in u_range:
28         # Numerical integration with error handling
29         result, _ = quad(exact, -np.inf, np.inf, args=(a_val,
      u_val), limit=100)
30         exact_results[a_val].append(result)
31
32         # GBF approximate integral with error handling
33         gbf_approx_val = approximant(a_val, u_val)
34         approx_results[a_val].append(gbf_approx_val)
35
36 # Plot the results with error handling and customized colors
37 plt.figure(figsize=(12, 8))
38
39 # Define custom colors for clarity
40 colors = ['red', 'green', 'blue']
41
42 for idx, a_val in enumerate(a_values):
43     actual_color = colors[idx]  # Color for the actual
      integral
44     gbf_color = colors[idx] + '--'  # Dashed line color for
      GBF approximation
45
46     plt.plot(u_range, exact_results[a_val], label=f'Actual
      Integral (a = {a_val})', color=actual_color, linestyle='-'
      , marker='')
47     plt.plot(u_range, approx_results[a_val], label=f'GBF
      Approximation (a = {a_val})', color=actual_color,
      linestyle='--', marker='')
48
49 # make a limit on the vertical axis
```

```
50  plt.ylim(2, 5)
51  plt.xlabel('u values')
52  plt.ylabel('Integral $I$')
53  plt.title('Comparison of Actual and GBF Approximate Integral
        for Different a Values (with customized colors)')
54  plt.legend()
55  plt.grid(True)
56  plt.savefig('gbf_approximation.png')
```

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.

As can be seen from the plot, thhe approximate integral is less accurate for more negative values of a on a range of u values.

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

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

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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.

We can use the definition for the free energy:

$$F = E - TS \tag{11}$$

The energy for a given molecule is given by:

$$E = -\varepsilon \sum_{i,j} \vec{\sigma}_i \cdot \vec{\sigma}_j \tag{12}$$

where the sum is over nearest neighbors. Now, we only care about the average value of this product, which is given by the expansion:

$$\sigma^2 \equiv \vec{\sigma}_i \cdot \vec{\sigma}_j = \langle \sigma_x \rangle^2 + \langle \sigma_y \rangle^2 + \langle \sigma_z \rangle^2 \tag{13}$$

We know that the value of $\langle \sigma_z \rangle$ is given by:

$$\langle \sigma_z \rangle = \frac{1}{3}(1 + 2S) \tag{14}$$

We can use this to find the value of $\langle \sigma_x \rangle$ and $\langle \sigma_y \rangle$ with the constraint that $\langle \sigma_x \rangle + \langle \sigma_y \rangle + \langle \sigma_z \rangle = 1$:

$$\langle \sigma_x \rangle = \frac{1}{3}(1 - S) \tag{15}$$

So, the σ^2 term is given by:

$$\sigma^2 = \frac{1}{9}(1 - S)^2 + \frac{1}{9}(1 - S)^2 + \frac{1}{9}(1 + 2S)^2 = \frac{1}{3}(1 + 2S^2) \tag{16}$$

We plug this value into the above summation for the energy, multiply by a factor of N since there are N molecules, also motive by a factor of the coordination number z, and divide by 2 to take into account over counting. We get:

$$E = -\frac{Nz\varepsilon}{6}(1 + 2S^2) \tag{17}$$

Next, we want to find the entropy. It is given by:

$$S = -k_B \sum_i^N \left(\langle \sigma_x \rangle \ln \langle \sigma_x \rangle + \langle \sigma_y \rangle \ln \langle \sigma_y \rangle + \langle \sigma_z \rangle \ln \langle \sigma_z \rangle \right) \quad (18)$$

We can use the values of $\langle \sigma_x \rangle$, $\langle \sigma_y \rangle$, and $\langle \sigma_z \rangle$ to find the value of the entropy. We get:

$$S = -k_B N \left(\frac{1-S}{3} \ln \frac{1-S}{3} + \frac{1-S}{3} \ln \frac{1-S}{3} + \frac{1+2S}{3} \ln \frac{1+2S}{3} \right) \quad (19)$$

Combining the 2 terms that are the same, we get:

$$S = -k_B N \left(\frac{2-2S}{3} \ln \frac{1-S}{3} + \frac{1+2S}{3} \ln \frac{1+2S}{3} \right) \quad (20)$$

So the total free energy is given by:

$$F = -\frac{Nz\varepsilon}{6}(1+2S^2) + k_B T N \left(\frac{2-2S}{3} \ln \frac{1-S}{3} + \frac{1+2S}{3} \ln \frac{1+2S}{3} \right) \quad (21)$$

Then, we simply have to divide by a factor of N to get the free energy per molecule:

$$f = -\frac{z\varepsilon}{6}(1+2S^2) + k_B T \left(\frac{2-2S}{3} \ln \frac{1-S}{3} + \frac{1+2S}{3} \ln \frac{1+2S}{3} \right) \quad (22)$$

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?

The main task now is to Taylor expand the natural logarithms in our free energy expression up to 4th order in S.

$$\ln \frac{1-S}{3} = \ln(1-S) - \ln 3 = -\ln 3 - S - \frac{S^2}{2} - \frac{S^3}{3} - \frac{S^4}{4} - \ldots \quad (23)$$

$$\ln \frac{1+2S}{3} = \ln(1+2S) - \ln 3 = -\ln 3 + 2S - \frac{4S^2}{2} + \frac{8S^3}{3} - \frac{16S^4}{4} + \ldots \quad (24)$$

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For the free energy, this gives:

$$f \approx \frac{S^4 T k_B}{2} - \frac{S^3 T k_B}{3} + S^2 T k_B - \frac{S^2 \epsilon z}{3} - T k_B \log{(3)} - \frac{\epsilon z}{6} + O(S^5) \quad (25)$$

This is a first order transition, as there is no term in S in the free energy expression.

```
from sympy import *

# Define the symbols for this expression: f = -\frac{z\
    varepsilon}{6} (1 + 2S^2) + k_B T \left(\frac{2 - 2S}{3} \
    ln \frac{1 - S}{3} + \frac{1 + 2S}{3} \ln \frac{1 + 2S
    }{3}\right)
f, z, S, T, epsilon, k_B = symbols('f z S T \epsilon k_B')
f = -z * epsilon / 6 * (1 + 2 * S**2) + k_B * T * ((2 - 2 * S
    ) / 3 * log((1 - S) / 3) + (1 + 2 * S) / 3 * log((1 + 2 *
    S) / 3))
# use this tailor expansion for the logarithm \ln \frac{1 - S
    }{3} = \ln (1 - S) - \ln 3 = -\ln 3 - S - \frac{S^2}{2} -
    \frac{S^3}{3} - \frac{S^4}{4} - \ldots and \ln \frac{1 + 2
    S}{3} = \ln (1 + 2S) - \ln 3 = -\ln 3 + 2S - \frac{4S
    ^2}{2} + \frac{8S^3}{3} - \frac{16S^4}{4} + \ldots
f = f.subs(log((1 - S) / 3), -log(3) - S - S**2 / 2 - S**3 /
    3 - S**4 / 4)
f = f.subs(log((1 + 2 * S) / 3), -log(3) + 2 * S - 4 * S**2 /
    2 + 8 * S**3 / 3 - 16 * S**4 / 4)
# simplify the expression
f = simplify(f)
# print the expression
print(latex(f))
```

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.)

For a first order transition, we know that

$$\frac{\partial f}{\partial S}(S^*, T^*) = \frac{\partial f}{\partial S}(0, T^*) \quad (26)$$

and we know that $F(S^*, T^*) = F(0, T^*)$. We can use these two equations to solve for T^* and S^*. Minimizing our free and energy with respect to the order perimeter gives:

$$-\frac{25S^4 T k_B}{2} + 2S^3 T k_B - S^2 T k_B + 2ST k_B - \frac{2S\epsilon z}{3} \quad (27)$$

3

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

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

3.1

(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

$$p = -\frac{1}{2}zJ + h - f \quad (6)$$

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

We see that the chemical potential relates to the magnetic field and ε_0 relates to the coupling constant J, giving a one-to-one correspondence between the Hamiltonians of the lattice gas and the Ising model. With the icing model at a certain site we had a choice of two spins $s_i = \pm 1$. Whereas for the lattice gas we have a choice of two states $\sigma_i = 0, 1$. These can be related by considering the following transformation:

$$\sigma_i = \frac{1}{2}(1 + s_i) \quad (28)$$

We can plug this into the partition function that was given for the lattes gas model:

$$\Xi = \sum_{\{\sigma_i\}} \exp\left\{\beta\mu \sum_i \sigma_i + \beta\varepsilon_0 \sum_{\langle ij \rangle} \sigma_i\sigma_j\right\} \quad (29)$$

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to get:

$$\Xi = \sum_{\{s_i\}} \exp\left\{\beta\mu \sum_i \frac{1}{2}(1+s_i) + \beta\varepsilon_0 \sum_{\langle ij\rangle} \frac{1}{4}(1+s_i)(1+s_j)\right\} \tag{30}$$

We take out the constant from inside the summation in both cases and do a distributive multiplication on the second term:

$$\Xi = \sum_{\{s_i\}} \exp\left\{\frac{1}{2}\beta\mu\left(\sum_i 1 + \sum_i s_i\right) + \frac{1}{4}\beta\varepsilon_0\left(\sum_{\langle ij\rangle} 1 + \sum_{\langle ij\rangle} s_i + \sum_{\langle ij\rangle} s_j + \sum_{\langle ij\rangle} s_i s_j\right)\right\} \tag{31}$$

Given that the total volume of one lattes site is 1, we can define the sum over all volumes as M:

$$M = \sum_i 1 \tag{32}$$

and then if we want to consider all interrupting pears, we have:

$$\sum_{\langle ij\rangle} 1 = \frac{1}{2}zM \tag{33}$$

where z is the coordination number and we divide by 2 to avoid over counting. Then we can write the partition function as:

$$\Xi = \sum_{\{s_i\}} \exp\left\{\frac{1}{2}\beta\mu M + \frac{1}{2}\beta\mu \sum_i s_i + \frac{1}{8}\beta\varepsilon_0 zM + \frac{1}{4}\beta\varepsilon_0 \sum_{\langle ij\rangle} s_i + \frac{1}{4}\beta\varepsilon_0 \sum_{\langle ij\rangle} s_j + \frac{1}{4}\beta\varepsilon_0 \sum_{\langle ij\rangle} s_i s_j\right\} \tag{34}$$

We recognise that the the sums $\sum_{\langle ij\rangle} s_i$ and $\sum_{\langle ij\rangle} s_j$ is just the sum of all the spins $\sum_i s_i$, and we can write the partition function as:

$$\Xi = \sum_{\{s_i\}} \exp\left\{\frac{1}{2}\beta\mu M + +\frac{1}{8}\beta\varepsilon_0 zM + \left(\frac{1}{2}\beta\mu + \frac{1}{4}\beta\varepsilon_0 z\right)\sum_i s_i + \frac{1}{4}\beta\varepsilon_0 \sum_{\langle ij\rangle} s_i s_j\right\} \tag{35}$$

Then, we know that the friend potential can be given by:

$$W = -\frac{1}{\beta}\ln\Xi = -pV \tag{36}$$

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where p is the pressure and V is the volume. We can use this to find the pressure:

$$p = \frac{1}{V}\frac{1}{\beta}\ln\Xi \tag{37}$$

But we know that the total volume is given by $V = M$, and we can use this to find the pressure:

$$p = \frac{1}{M}\frac{1}{\beta}\ln\Xi \tag{38}$$

We can use the expression for the partition function to find the pressure:

$$p = \frac{1}{M}\frac{1}{\beta}\ln\sum_{\{s_i\}}\exp\left\{\frac{1}{2}\beta\mu M + +\frac{1}{8}\beta\varepsilon_0 zM + \left(\frac{1}{2}\beta\mu + \frac{1}{4}\beta\varepsilon_0 z\right)\sum_i s_i + \frac{1}{4}\beta\varepsilon_0\sum_{\langle ij\rangle} s_i s_j\right\} \tag{39}$$

We can remove the first two terms from the exponent as they do not depend on s_i:

$$p = \frac{1}{M}\frac{1}{\beta}\left(\frac{1}{2}\beta\mu M + \frac{1}{8}\beta\varepsilon_0 zM\right) + \frac{1}{M}\frac{1}{\beta}\ln\sum_{\{s_i\}}\exp\left\{\left(\frac{1}{2}\beta\mu + \frac{1}{4}\beta\varepsilon_0 z\right)\sum_i s_i + \frac{1}{4}\beta\varepsilon_0\sum_{\langle ij\rangle} s_i s_j\right\} \tag{40}$$

Making cancellations for the two terms not in the submission gives:

$$p = \frac{1}{2}\mu + \frac{1}{8}\varepsilon_0 z + \frac{1}{M}\frac{1}{\beta}\ln\sum_{\{s_i\}}\exp\left\{\left(\frac{1}{2}\beta\mu + \frac{1}{4}\beta\varepsilon_0 z\right)\sum_i s_i + \frac{1}{4}\beta\varepsilon_0\sum_{\langle ij\rangle} s_i s_j\right\} \tag{41}$$

Comparing to the icing model, we see that the end along of the magnetic field h is given by:

$$h = \frac{1}{2}\mu + \frac{1}{4}\varepsilon_0 z \tag{42}$$

and then the analogue for the two body interaction J is given by:

$$J = \frac{1}{4}\varepsilon_0 \tag{43}$$

In the icing model, the free energy per spin is given by:

$$f = -\frac{\ln Z}{\beta M} \tag{44}$$

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with Z given by:

$$Z = \sum_{\{s_i\}} \exp \left\{ (\beta h) \sum_i s_i + \beta J \sum_{\langle ij \rangle} s_i s_j \right\} \tag{45}$$

Putting this all together, we see that the pressure is given by:

$$p = \frac{\mu}{2} + \frac{\varepsilon_0 z}{8} - f \tag{46}$$

Substituting in the values for h and J gives:

$$p = -\frac{1}{2} z J + h - f \tag{47}$$

3.2

(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).

The random mixing approximation essentially means that we have:

$$\langle \sigma_i \rangle = \frac{n}{M} = \sigma_i = \rho \tag{48}$$

where n is the number of particles and M is the total number of lattice sites. Our initial partition function is given by:

$$\Xi(\mu, V, T) = \sum_{\{\sigma_i\}} \exp \left\{ \beta\mu \sum_i \sigma_i + \beta\varepsilon_0 \sum_{\langle ij \rangle} \sigma_i \sigma_j \right\} \tag{49}$$

the first submission inside of the exponent is just ρ some over all of the that is sits, so this term just becomes $\beta\mu\rho M$. The second term is a submission over all of the nearest pairs, so this contributes a factor of $\frac{1}{2}\beta z \varepsilon_0 \rho^2 M$, where we have divided by 2 to avoid over counting. The partition function is then given by:

$$\Xi(\mu, V, T) = \sum_{\{\sigma_i\}} \exp \left\{ \beta\mu\rho M + \frac{1}{2}\beta z \varepsilon_0 \rho^2 M \right\} \tag{50}$$

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The initial sum overall lattes are curation can be thought of as choosing that number of ways to put n particles into M sites, and this is given by the binomial coefficient:

$$\Xi(\mu, V, T) = \sum_{n=0}^{M} \binom{M}{n} \exp\left\{\beta\mu\rho M + \frac{1}{2}\beta z\varepsilon_0\rho^2 M\right\} \tag{51}$$

We notice that $n = \rho M$, and we can use this to write the partition function as:

$$\Xi(\mu, V, T) = \sum_{n=0}^{M} \frac{M!}{\rho M!(M - \rho M)!} \exp\left\{\beta\mu M\rho + \frac{1}{2}\beta z\varepsilon_0\rho^2 M\right\} \tag{52}$$