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Statistical Mechanics

PHYS 5163 Homework Assignment 8

Problems: {1, 2, 3, 4}

Due: April 18, 2022 at 6:00 PM

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Problem 1:

This is a quantum statistical mechanics problem.

Consider N identical bosons, each of which is treated as an isotropic three-dimensional harmonic oscillator. Using the recursion relation from P. Borrmann and G. Franke, J. Chem. Phys. 98, 2484 (1993) [you can access this paper through the OU library] for the partition function in the canonical ensemble, write a little code that plots (or allows you to plot) the internal energy per particle as a function of the temperature for $N = 10$.

WARNING 1: I suggest that you test your code with $N = 2, 3, \cdots$ to get results quickly. For large N, the calculations may take hours (please do not run this for $N = 1{,}000$).

WARNING 2: If you set your loops up incorrectly, you might end up writing a code that runs infinitely long or eats up tremendous amounts of memory. Please carefully test your code to ensure that this is not happening.

Hint: How to approach this problem?

- Step 1: Find a compact analytical expression for $S(k)$ defined in Eq. (2) of the paper [you can get rid of the infinite sum(s)—note that the subscript j is hiding three infinite sums and note that k is an integer and not Boltzmann's constant...].
- Step 2: Implement the finite sum for $Z(N)$ given in Eq. (1) of the paper. Note that Z is used to denote the canonical partition function; in class, we used Q or Q_N . It can be recognized that $Z(N)$ is defined recursively—this is where you might encounter problems if your code is not set up correctly... To give you a sense, my Mathematica notebook is seven lines long/short.

The article that we were given tells us that

$$S(k) = \sum_j \exp(-\beta k \epsilon(j))$$

Where $\epsilon(j)$ is defined as

$$\epsilon(j) = \left(n_j + \frac{3}{2}\right)\hbar\omega$$

This then makes $S(k)$

$$S(k) = \sum_j \exp(-\beta k(n_j + 3/2)\hbar\omega) = \exp(-3/2\, \beta k \hbar\omega) \sum_j \exp(-\beta k n_j \hbar\omega)$$

If we then expand n_j, we have

$$n_j = n_x + n_y + n_z \doteq 3n$$

This then means $S(k)$ becomes

$$S(k) = \sum_{n=0} \exp(-3/2\, \beta k \hbar\omega) \exp(-\beta k(3n)\hbar\omega)$$
$$= \sum_{n=0} \exp(-1/2 \beta k \hbar\omega)^3 \exp(-\beta k n \hbar\omega)^3$$

Problem 1: Continued

$$= \left(\exp(-\tfrac{1}{2}\beta k \hbar\omega) \sum_{n=0} \exp(-\beta k \hbar\omega)^n \right)^3$$

$$= \left(\exp(-\tfrac{1}{2}\beta k \hbar\omega) \sum_{n=1} \exp(-\beta k \hbar\omega)^{n-1} \right)^3$$

We now have $s(k)$ in a geometric series representation

$$\sum_{n=1} a \cdot r^{n-1} = \frac{a}{1-r}$$

Which for us becomes

$$s(k) = \left(\frac{\exp(-\tfrac{1}{2}\beta k \hbar\omega)}{1-\exp(-\beta k \hbar\omega)} \right)^3 = \left(\frac{1}{2\sinh(\tfrac{1}{2}\beta k \hbar\omega)} \right)^3 = \frac{\operatorname{csch}^3(\tfrac{1}{2}\beta k \hbar\omega)}{8}$$

We now have a compact equation for $s(k)$

$$s(k) = \frac{\operatorname{csch}^3(\tfrac{1}{2}\beta k \hbar\omega)}{8}$$

The partition function is then

$$Q_N = \sum_{n=1}^{N} \frac{1}{N} s(n) \cdot Q(N-n)$$

Where we initiall set $Q(0) = 1$. In order to plot this we say

$$\operatorname{csch}^3(\tfrac{1}{2}\beta k \hbar\omega) \rightarrow \operatorname{csch}^3(\tfrac{1}{2}\beta k)$$

Where $\hbar\omega$, and Boltzmann's constant k are 1. We now calculate the internal energy with

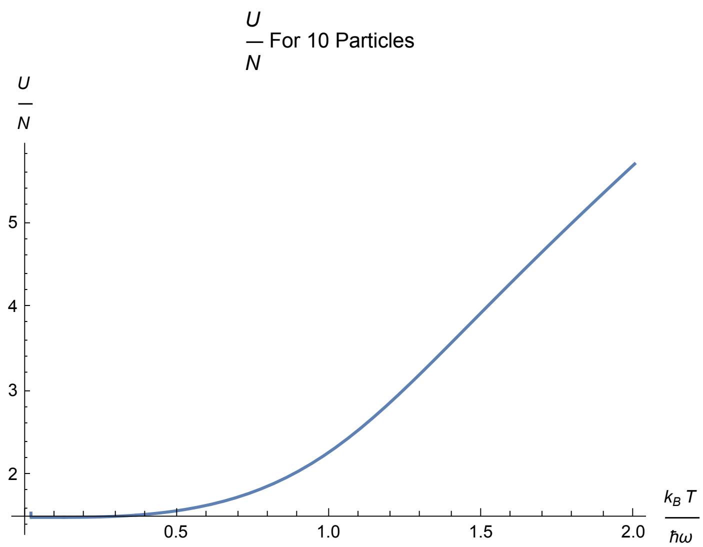
$$U = -\frac{\partial}{\partial\beta}(Q_N)$$

The rest of this problem will be done in Mathematica.

In[41]:=

```
Q[0] = 1;
S[k_] := 1/8 * Csch[(β * k)/2]^3;
Q[n_] := 1/n * Sum[S[k] * Q[n - k], {k, 1, n}];
U[n_] := -D[Log[Q[n]], β];
InternalEnergyPer[n_] := (U[10] /. β → 1/T)/n;
Quiet[Plot[InternalEnergyPer[10], {T, 0, 2},
  PlotLabel → "U/N For 10 Particles", AxesLabel → {"k_B T/ħω", "U/N"}]]
```

Out[46]=



Problem 1: Review

Procedure:

- - Begin with the equation for entropy
$$S(k) = \sum_j \exp\left(-\beta k \epsilon(j)\right)$$
that was given in the article
  - Define $\epsilon(j)$ and put this back into the equation for entropy
  - Substitute in a geometric series
$$\sum_{n=1} ar^{n-1} = \frac{a}{1-r}$$
into the expression for entropy to get rid of the infinite sum that is present
  - Use the equations for the partition function and the internal energy
$$U = -\frac{\partial}{\partial \beta}(Q_N)$$
to plot this in Mathematica
  - See Mathematica code to see how to graph this

Key Concepts:

- - This problem is showing us how a paper was able to make the plots that it had as well as how to derive some of results analytically
  - We see from the plot that as temperature increases the internal energy of our particles will increase

Variations:

- - This problem is pretty concrete in that it cannot change unless the entire problem is to change
  - The only applicable change to this would be to use a different number of particles for the internal energy
    * This would just change the number of particles we would put into Mathematica. Everything up to this point would be the exact same

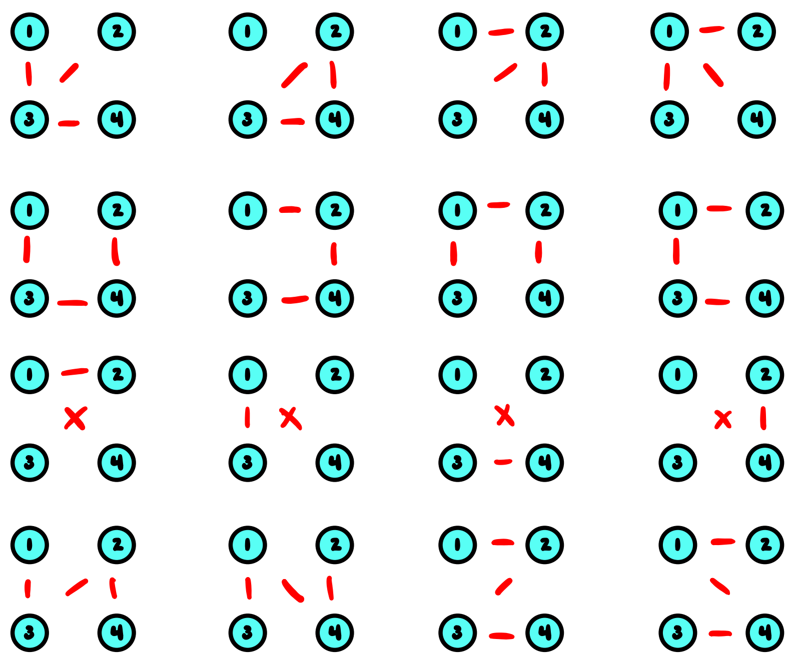
Problem 2:

In class we discussed configuration integrals. For three particles, e.g., there exist four different configuration integrals, three with two "connections" (two of the "circled" 1, 2, and 3 are connected) and one with three "connections" (the three "circled" 1, 2, and 3 are connected). We can refer to this loosely as two "topologically distinct" classes, containing respectively three graphs and one graph.

For four particles, work out the number of topologically distinct classes as well as the number of graphs per class. Do not just write down your answers—please also explain how you arrived at your answers.

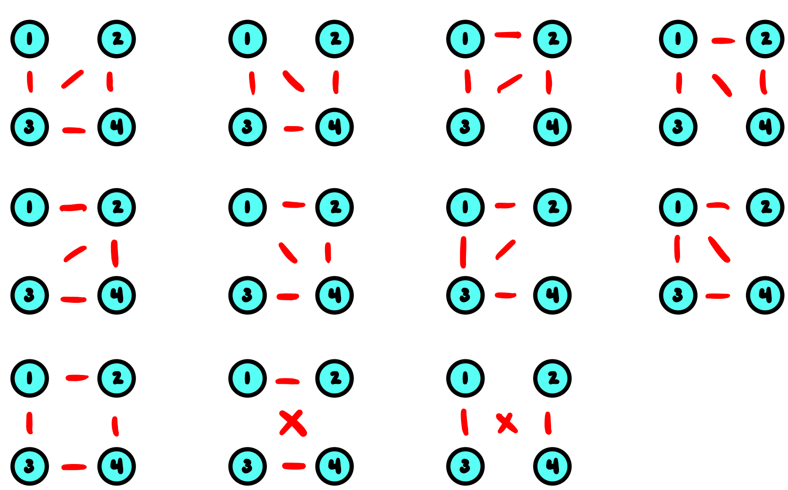
For four particles, we need at least 3 connections going up to 6. Starting with 3 we count

3 connections :



Where For 3 connections we have 16 possibilities. For 4 connections we then have

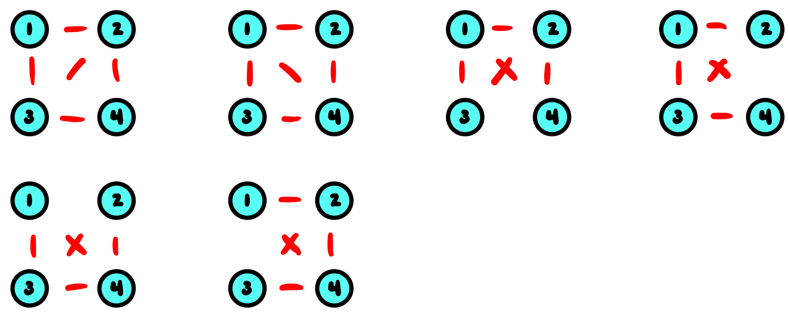
4 connections :



Problem 2: Continued

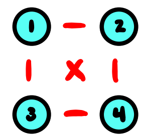
Which totals up to be 11 possibilities. If we then count the combinations for 5 connections we have

5 connections :



Where we have 6 possibilities. Lastly, for 6 connections we only have

6 connections :



1 possibility for 6 connections. We then finally have 34 classes and they are classified with different shapes.

If we categorize these by classes we find

Class 1 : (2N w 2E , 2N w 1E) : 12 possibilities

Class 2 : (1N w 3E , 3N w 1E) : 4 possibilities

Class 3 : (1N w 3E , 2N w 2E , 1N w 1E) : 12 possibilities

Class 4 : (4N w 4E) : 3 possibilities

Class 5 : (2N w 3E , 2N) : 6 possibilities

Class 6 : (4N w 3E) : 1 possibility

Problem 2: Review

Procedure:

- - Begin by drawing four particles in the shape of a square and then drawing interactions between the particles for 3, 4, 5, and 6 connections
  - Count all the connections and then categorize them

Key Concepts:

- - For four particles, there has to be a minimum of 3 connections among the particles for it to be possible
  - The maximum number of connections can be 6 for four particles
  - As the number of connections between our particles increases, the number of topologically distinct classes decreases

Variations:

- - The number of particles could change
    * This would require us to find the new minimum and maximum number of connections that are required / possible for this ensemble. After this we would repeat the same procedure as before

Problem 3:

This problem considers the cluster expansion using classical statistical mechanics.

(a) Calculate a_2 for the hard sphere potential, which is given by $v(r) = \infty$ for $r < \sigma$ and $v(r) = 0$ otherwise.

We calculate a_2 with the hard sphere potential

$$a_2 = \frac{2\pi}{\lambda^3}\int_0^\infty (1 - e^{-\beta v(r)}) r^2 \, dr$$

$$= \frac{2\pi}{\lambda^3}\left(\int_0^\sigma r^2(1 - \cancelto{0}{e^{-\beta\infty}}) dr + \int_\sigma^\infty r^2 \cancel{(1 - e^{-\beta(0)})} dr\right)$$

$$= \frac{2\pi}{\lambda^3}\int_0^\sigma r^2 dr = \frac{2\pi}{3\lambda^3} r^3 \Big|_0^\sigma = \frac{2\pi\sigma^3}{3\lambda^3}$$

This means

$$\boxed{a_2 = \frac{2\pi\sigma^3}{3\lambda^3}}$$

(b) Calculate a_2 for the square well potential, which is given $v(r) = \infty$ for $r < \sigma$, $v(r) = -\epsilon$ for $\sigma \leq r \leq a\sigma$ ($\epsilon > 0$ and $\alpha > 1$), and $v(r) = 0$ otherwise.

We repeat the same process as (a) but with different conditions

$$a_2 = \frac{2\pi}{\lambda^3}\left(\int_0^\infty r^2(1 - e^{-\beta v(r)}) dr\right)$$

This changes to

$$a_2 = \frac{2\pi}{\lambda^3}\left(\int_0^\sigma r^2(1 - \cancelto{0}{e^{-\beta\infty}}) dr + \int_\sigma^{\alpha\sigma} r^2(1 - e^{-\beta(-\epsilon)}) dr\right)$$

$$= \frac{2\pi}{\lambda^3}\left(\frac{\sigma^3}{3} + \int_\sigma^{\alpha\sigma} r^2(1 - e^{\beta\epsilon}) dr\right) = \frac{2\pi}{\lambda^3}\left(\frac{\sigma^3}{3} + \frac{\sigma^3}{3}(1 - e^{\beta\epsilon})(\alpha^3 - 1)\right)$$

$$= \frac{2\pi}{\lambda^3}\frac{\sigma^3}{3}\left(1 + (\alpha^3 - 1)(1 - e^{\beta\epsilon})\right)$$

So our final answer is

$$\boxed{a_2 = \frac{2\pi}{\lambda^3}\frac{\sigma^3}{3}\left(1 + (\alpha^3 - 1)(1 - e^{\beta\epsilon})\right)}$$

Problem 3: Continued

(c) What are realistic parameters for σ, ϵ, and α? And how do you know? What is the temperature regime in which you might expect the description to work reasonably well.

It would be reasonable for σ to be around the size of the diameter of our particle.

ϵ is the strength of our interactions so as it grows we can expect our total potential energy to grow. This sets α to just be > 1.

I would expect this to work well in a high temp regime where $kT \approx \epsilon$.

Problem 3: Review

Procedure:

- – Begin by calculating a_2 by integrating the hard sphere potential over all space

$$a_2 = \frac{2\pi}{\lambda^3}\int_0^\infty (1-\exp(-\beta V(r)))r^2\,dr$$

  and apply the conditions for $V(r)$ for the specific ranges of r

- – Repeat the same procedure found in part (a) for these new conditions in (b)
- – This part is purely qualitative so using deductive reasoning one can roughly estimate what these parameters should be

Key Concepts:

- – Here we split the integral into two parts where one component goes to zero in the integration
- – This has the same concepts as part (a) but with different values for the potential as the value of r changes thus yielding a different final answer
- – Due to the parameters that control the size of σ and ϵ we can deduce that this would work well in a regime for a few hundred Kelvin

Variations:

- –

Variations:

- – For both parts (a) and (b), we could be given a different potential to use for the integration for a_2 (i.e hard wall etc.)
    - ∗ This would change the function that we are integrating but not the limiting cases for $V(r)$
  - – We could be given different limiting cases for $V(r)$
    - ∗ We then use the same procedure but with these new limits
- – We could be asked some other qualitative questions
    - ∗ We then would refer to whatever equations that are necessary for us to answer these questions

Problem 4:

In looking at the virial equation of state, we faced the following mathematical problem. Given the expansions

$$x = t + a_2t^2 + a_3t^3 + ... \tag{1}$$

and

$$y = t + b_2t^2 + b_3t^3 + ..., \tag{2}$$

where $a_2, a_3, ...$ and $b_2, b_3, ...$ are assumed to be known, one needs the expansion coefficients A_n that appear in the expansion

$$y = x + A_2x^2 + A_3x^3 + ...$$

Task of this problem: Obtain explicit expressions for A_2, A_3, and A_4. Note: Obtaining expressions for all An is, in general, non-trivial.

Starting with

$$y = x + A_2x^2 + A_3x^3 + A_4x^4 \qquad (*)$$

where the following equations come from mathematica (ignoring powers of 5 or higher)

$$y = t + (A_2+a_2)t^2 + (a_3 + 2a_2A_2 + A_3)t^3 + (a_4 + a_2^2A_2 + 2a_3A_2 + 3a_2A_3 + A_4)t^4 + \mathcal{O}(t^5) \qquad (**)$$

we then compare the powers of t above with those in equation (2)

$$y = t + b_2t^2 + b_3t^3 + b_4t^4 \qquad (***)$$

we then compare $(**)$ and $(***)$ to show A_2 is,

$$A_2 + a_2 = b_2 \quad \therefore \quad A_2 = b_2 - a_2$$

A_3 is then,

$$a_3 + 2a_2(b_2-a_2) + A_3 = b_3 \quad \Rightarrow \quad A_3 = b_3 - a_3 - 2a_2(b_2-a_2)$$

Where finally A_4 is

$$a_4 + (b_2-a_2)(a_2^2+2a_3) + 3a_2(b_3-a_3-2a_2(b_2-a_2)) + A_4 = b_4$$

$$\Rightarrow \quad A_4 = b_4 - a_4 - (b_2-a_2)(a_2^2+2a_3) - 3a_2(b_3-a_3-2a_2(b_2-a_2))$$

$$\boxed{\begin{aligned} &A_4 = b_4 - a_4 - (b_2-a_2)(a_2^2+2a_3) - 3a_2(b_3-a_3-2a_2(b_2-a_2)) \\ &A_3 = b_3 - a_3 - 2a_2(b_2-a_2) \\ &A_2 = b_2 - a_2 \end{aligned}}$$

In[14]:= $x = t + a_2 * t^2 + a_3 * t^3 + a_4 * t^4;$

$y = x + A_2 * x^2 + A_3 * x^3 + A_4 * x^4;$

In[17]:= Series[Collect[y, t], {t, 0, 4}]

Out[17]= $t + (a_2 + A_2)\, t^2 + (a_3 + 2\, a_2\, A_2 + A_3)\, t^3 + \left(a_4 + a_2^2\, A_2 + 2\, a_3\, A_2 + 3\, a_2\, A_3 + A_4\right) t^4 + O[t]^5$

Problem 4: Review

Procedure:

- - Begin by putting in equation (1) into the last expression for y and collecting the terms for the powers of t
  - Take the previous expression and compare it to equation (2) to find an expression for A_2
  - With the comparison of equation (2) and the first equation we produced, we can find the other variables like A_3 and A_4 by finding them recursively with one another

Key Concepts:

- - This is purely a mathematical problem to show us that we can take two equations (equation (2) and the last equation for y) and compare them since they represent the same value
    * We can then use this to deduce the coefficients like A_2 and etc.

Variations:

- - We could be given a different system of equations to work with
    * We then use the same broad procedure to find the other coefficients