

Problem Set PS08
Issued: 10/24/02 Due: 10/31/02

Prof. Darin J. Ulness

Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. The trace of a matrix M (written $\text{Tr}[M]$) is simply the sum of the diagonal elements of M . By diagonal one means top left to bottom right. Evaluate the trace for the following matrices.

(a)

$$M = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

(b)

$$M = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

2. Associated with matrices are eigenvectors and eigenvalues. These are analogues of the eigenfunctions and eigenvalues we have worked with for operators. That is, the column vector V is an eigenvector of the matrix M corresponding to the eigenvalue λ if

$$MV = \lambda V.$$

We will not learn how to calculate eigenvectors and eigenvalues in this course (if you had linear algebra you did quite a lot of this), but Mathematica can quickly calculate eigenvectors and eigenvalues. Use Mathematica to determine the eigenvectors and eigenvalues of the following matrices. Comment on your answer for (b) also compare the sum of the eigenvalues for parts (a) and (b) to the answers you got for the traces in the preceding problem.

(a)

$$M = \begin{bmatrix} 1 & -1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

(b)

$$M = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{bmatrix}$$

3. The geometric series is defined as

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \dots$$

As you perhaps learned in your Algebra II or pre-calc class in high school, this series can, in fact, be written in closed form as

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}.$$

(a) For what values of x is this series valid?

(b) Write

$$a + af(r) + af(r)^2 + af(r)^3 + \dots,$$

where $f(r)$ is some arbitrary function of r , in closed form and in series notation (i.e., \sum notation).

(c) Write

$$1 + af(r) + a^2f(r)^2 + a^3f(r)^3 + \dots,$$

in closed form and in series notation.

(d) Write

$$1 + e^{-\beta x} + e^{-2\beta x} + e^{-3\beta x} + \dots$$

in closed form and in series notation. Convince yourself that the closed form expression is valid for all positive x when $\beta > 0$.

Exercises

4. A vial containing 10^{20} oxygen molecules is at 300K. How many molecules are in each of the first four vibrational states assume the harmonic oscillator model applies. (The stretching mode of oxygen is 1580cm^{-1}). Note we will often need to know the so-called thermal energy (kT) in units of wavenumbers. You may want to download my kT calculator from the "files to download" section of the PChem website.
5. Derive the closed form canonical partition function for an ensemble of harmonic oscillators,

$$q_{HO} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}},$$

from the series representation. Also show $q_{HO} = \frac{1}{2\sinh\frac{1}{2}\beta\hbar\omega}$. Finally separately plot q_{HO} as a function of temperature and then as a function of frequency. What do each of these plots mean physically? (It might be helpful to check out Castro's legacy project from four years ago)

- Express the complete closed form partition function for a mole of oxygen gas? (Hint: this is a simple problem, don't read too much into it).
- Later on we will derive a relation between pressure, P , and the partition function to be

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Q}{\partial V} \right)_{n,\beta}.$$

For an ideal monatomic gas we have to worry only about translation of the gas in its container (volume V). Thus the partition function is (ignoring the $1/N!$ factor)

$$Q = q_{\text{mol}}^N = q_{\text{trans}}^N.$$

Using the translational partition function given on p77 of the notes, derive the ideal gas law. Note: the gas constant $R = N_A k$ where N_A is Avogadro's number. Also the number of moles is $n = N/N_A$. Why don't we need to worry about the $1/N!$ factor? (Hint: think about the properties of logs).

- Consider the j^{th} particle of an ideal gas in a 3D cubic box (length a for each dimension) of volume $V = a^3$. Next semester we will solve the Schrödinger equation for this problem and find that the energy which now is described by three quantum numbers is

$$E_{n_x, n_y, n_z}^{(j)} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2).$$

The contribution that the j^{th} particle makes to the total pressure is given by

$$P^{(j)} = - \frac{dE_{n_x, n_y, n_z}^{(j)}}{dV}.$$

That is to say, the pressure is given by the amount of energy it takes to change the volume. Use the equation $V = a^3$ and the chain rule to show

$$P^{(j)} = \frac{2E_{n_x, n_y, n_z}^{(j)}}{3V}.$$

Expressing this equation as an average one has

$$\bar{P} = \frac{2\bar{E}}{3V}.$$

We will learn in thermodynamics that $\bar{E} = \frac{3}{2} NkT$ for an ideal gas of N particles. Use this to obtain the ideal gas law (note $Nk = nR$, verify this).

- Consider some crazy quantum system consisting of three energy levels $\varepsilon_1 = 0$, $\varepsilon_2 = E$ and $\varepsilon_3 = 3E$.
 - Write out the partition function, q_{crazy} , for an ensemble of these systems.
 - Calculate the ensemble averaged energy.

10. Consider a very intense laser excitation of matter such that the light–matter interaction is nonlinear: $\mu(t) = \alpha(t)E(t)^3$. Derive a nonlinear scattering equation analogous to Eq. (5.4) of the notes. Use trig identities to simplify the expression such that all the scattering frequencies are easily identified. These scattered frequencies are called third order processes. A number of processes occur at third order. These include (i) third harmonic generation, (ii) degenerate four wave mixing, (iii) coherent Stokes Raman scattering (CSRS pronounced scissors), (iv) coherent anti-Stokes Raman scattering (CARS) and some unnamed processes. Use your intuition to assign each of your derived frequencies to one of these processes.
11. I have mentioned in class that statistical mechanics preceded quantum mechanics. You might wonder how that can be since the energy levels from quantum mechanics appear explicitly in the Boltzmann distribution and in the canonical partition function. In fact one can define a classical Boltzmann distribution which describes the probability of finding a particle at position x with momentum p as

$$\frac{e^{-\beta H_{cl}(x,p)}}{Q} = \frac{e^{-\beta T_{cl}(p)} e^{-\beta V_{cl}(x)}}{Q},$$

where

$$Q = \int \int e^{-\beta H_{cl}(x,p)} dp dx$$

Let us apply this to a classical 1D harmonic oscillator where for a single oscillator $T_{cl} = \frac{p^2}{2m}$ and $V_{cl}(x) = \frac{kx^2}{2}$.

(a) Use Mathematica to show

$$q_{HO} = \int \int e^{-\beta T_{cl}(p)} e^{-\beta V_{cl}(x)} = \frac{2\pi}{\beta\omega},$$

where $\omega = \sqrt{k/m}$ is the frequency of the harmonic oscillator.

- (b) Plot the Boltzmann distribution in what is called phase space in which p is the y -axis and x is the x -axis. Generate a plot for $k = m = 1$ and $\beta = 1$. Then generate a plot for $k = m = 1$ and $\beta = 3$. Use the same scale for the axes for each of these plots. Identify which of these plots correspond to the higher temperature. Also try to explain what the phase space plot is telling us.

Conceptual Problems

12. The thermal de Broglie wavelength is a measure of the “quantumness” of the ensemble. That is how much quantum character is manifest in the macroscopic system. Plot the thermal de Broglie wavelength as a function of temperature. What does this say about the quantumness of the ensemble as a function of temperature? Superfluidity and superconductivity are very quantum in character. Based on you above argument, would you expect (macroscopic) superfluidity or superconductivity at high or low temperatures?

13. Using the classical theory of light scattering (Eq. (5.4) in the notes), sketch the Rayleigh, Stokes and anti-Stokes spectral lines for oxygen. Assume oxygen has one active mode (1580cm^{-1}) and assume the laser light used to do the scattering is at 20000cm^{-1} (this is 500nm — green light).

Computer Problems

14. Consider a linear chain of N atoms. Each of the atoms can be in one of four states A , B , C or D , except that an atom in state A can not be adjacent to an atom in state B and an atom in state B can not be adjacent to an atom in state C . Find the entropy per atom for this system as $N \rightarrow \infty$. To solve this problem it is useful to define the set of four dimensional column vectors $V^{(j)}$ such that the four elements are the total number of allowed configurations of a j -atom chain having the j^{th} atom in state A , B , C , or D . For example,

$$V^{(1)} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}, \quad V^{(2)} = \begin{bmatrix} 3 \\ 2 \\ 3 \\ 4 \end{bmatrix}, \quad V^{(3)} = \begin{bmatrix} 10 \\ 6 \\ 10 \\ 12 \end{bmatrix}, \dots$$

The $V^{(j+1)}$ can be found from the $V^{(j)}$ vector using the matrix equation,

$$V^{(j+1)} = MV^{(j)},$$

where for this example

$$M = \begin{bmatrix} 1 & 0 & 1 & 1 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 1 & 1 & 1 \end{bmatrix}.$$

The matrix M is the so-called transfer matrix for this system. It can be shown that the number of configurations $W = \text{Tr}[M^N]$. Now for large N , $\text{Tr}[M^N] \approx \lambda_{\text{max}}^N$, where λ_{max} is the largest eigenvalue of M . So

$$W = \lim_{N \rightarrow \infty} \lambda_{\text{max}}^N.$$

- Use M to find $V^{(4)}$ and $V^{(5)}$
- Verify $V^{(2)}$ explicitly by drawing all the allowed 2-atom configurations.
- Verify $W = \text{Tr}[M^N]$ for $N = 1$ and $N = 2$.
- Use Boltzmann's equation to find the entropy per atom for this chain as N goes to infinity.
- What is the entropy per atom for the case of $N = 4$. How does this compare to the large N answer.

15. Consider again the case of a linear chain having four possible monomer units A , B , C and D , but now the chain is formed such that A must always precede B , C and D ; B must always precede C and D ; and C must always precede D . The transfer matrix for this case is

$$M = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 1 \end{bmatrix}$$

- (a) Use M to find $V^{(2)}$, $V^{(3)}$, $V^{(4)}$ and $V^{(5)}$
(b) Verify $V^{(3)}$ by writing out all allowed three atom chains
(c) Use Boltzmann's equation to find the entropy per atom for this chain as N goes to infinity.

Reflective Exercises

16. Considering your future career, think of a task you may be called upon to do that will make the PChem oral exams seem trivial (e.g., Ph.D. defense or having to inform a mother that her child has leukemia, etc.). Do you feel that you have the strength to complete the task in a professional manner?

Extra Problem for PS08

1. Model the sun at noon and at dusk by using Mathematica and the following data on the percent of direct sunlight incident on the surface relative to the top of the atmosphere (from J.D. Jackson Classical Electrodynamics).

| Color | Noon | Dusk |
|-------|------|----------------------|
| red | 0.96 | 0.21 |
| green | 0.90 | 0.024 |
| blue | 0.76 | 6.5×10^{-5} |

For this to work you need to separately normalize each set of data such that red = 1, then type the following code (but replace the words "red," "green" and "blue" with their values):

- `<<Graphics<Graphics`
- `Show[Graphics[{RGBColor[red, green, blue], Disk[{0, 0}, 1]}], AspectRatio->1]`

Does the simulation jive with your experience?

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Does the simulation jive with your experience?

1 a) $Tr[M] = 1 + 1 + 1 = 3$

b) $Tr[M] = \lambda_1 + \lambda_2 + \lambda_3$

2 c) eigenvalues: 0, 1, 2

eigen vectors: $\begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix}, \begin{bmatrix} -1 \\ 1 \\ 1 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix}$

b) eigenvalues: $\lambda_1, \lambda_2, \lambda_3$

eigen vectors: $\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$

3 a) valid for $x \leq 1$

b) $\frac{a}{1-afcr}$

c) $\frac{1}{1-afcr}$

d) $\frac{1}{1-e^{-\beta x}}$ valid for all $x > 0$ if $\beta > 0$

4 $g_{H0} = \frac{1}{2 \sinh(\frac{1500}{200})}$

$N_0 = \frac{e^{-\frac{1500}{200}}}{2g_{H0}} = N_1 = \frac{e^{-\frac{3 \cdot 1500}{200}}}{2g_{H0}}$

$N_2 = \frac{e^{-\frac{5 \cdot 1500}{200}}}{2g_{H0}} = N_3 = \frac{e^{-\frac{7 \cdot 1500}{200}}}{2g_{H0}}$

5 see last year's soln.

6 $Q = \frac{1}{N_A} (2n_{trans} 2n_{rot} 2n_{vib})^{N_A} \quad N = N_A \text{ for 1 mole}$

$Q = \frac{1}{N_A} \left(\frac{V}{\Lambda^3} \frac{T}{2\theta_R} \frac{1}{2 \sin^2 \frac{\beta h \nu}{2}} \right)^{N_A}$

7 $z_N = \frac{V}{\Lambda^3} \quad Q = \left(\frac{V}{\Lambda^3} \right)^N$

$P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V} \quad \ln Q = \ln \left(\frac{V}{\Lambda^3} \right)^N = N \ln V - N \ln \Lambda^3$

$P = \frac{1}{\beta} \frac{\partial}{\partial V} (N \ln V - N \ln \Lambda^3) = \frac{N}{\beta V} = \frac{NkT}{V}$

$P = \frac{NkT}{V}$ The ideal gas law

8 $\beta^{(1)} = - \frac{d \ln Z_{trans}}{dV} = - \frac{d \ln \left(\frac{V}{\Lambda^3} \right)}{dV} = - \frac{1}{V}$

$\frac{d \ln Z}{d \ln a} = \frac{d \left(\frac{1}{\Lambda^3} (n_1^2 + n_2^2 + n_3^2) \right)}{d \ln a} = \frac{-2h^2}{8ma^2} (n_1^2 + n_2^2 + n_3^2)$

$\frac{d \ln Z}{dV} = \frac{1}{V} = \frac{1}{3a^2}$

so $\beta^{(1)} = - \left(- \frac{2h^2}{8ma^2} \right) \left(\frac{1}{3a^2} \right) = \frac{2h^2}{12ma^4}$

$\bar{P} = \frac{2}{3} \frac{E}{V} \quad \bar{E} = \frac{2}{3} NkT$

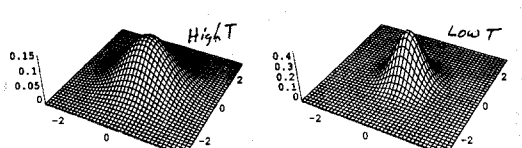
$\bar{P} = \frac{2}{3} \frac{2}{3} \frac{NkT}{V} \Rightarrow \bar{P} = \frac{NkT}{V}$ ideal gas law

9 $Z_{trans} = 1 + e^{-\beta \epsilon} + e^{-3\beta \epsilon}$
 $\bar{E} = \frac{1}{Z_{trans}} (0 + \epsilon e^{-\beta \epsilon} + 3\epsilon e^{-3\beta \epsilon}) = \frac{\epsilon}{Z_{trans}} \left(e^{-\beta \epsilon} + 3e^{-3\beta \epsilon} \right)$

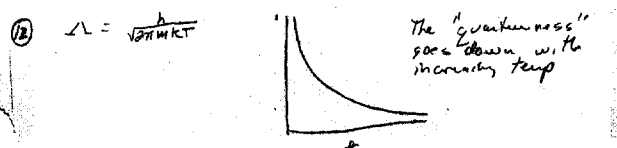
10 $N(x,t) = (a_0 + a_1 \cos \omega_R t) E_0 \cos \omega t + E_0 \cos \omega t + E_0 \cos \omega t$
 $N(x,t) = k_0 E_0^2 \cos \omega t \cos \omega t \cos \omega t + a_1 E_0^2 \cos \omega t + \cos \omega t \cos \omega t \cos \omega t$
 $= a_0 E_0^2 [\cos^3 \omega t + 3 \cos \omega t] + a_1 E_0^2 [\cos(3\omega - \omega_R)t + \cos(3\omega + \omega_R)t + \cos(\omega - \omega_R)t + \cos(\omega + \omega_R)t]$

frequency: $3\omega, \omega, \omega - \omega_R, \omega + \omega_R, \omega - \omega_R, \omega + \omega_R$
 process: $3rd \text{ harmonic generation, D4WM, CSRS, CARS}$

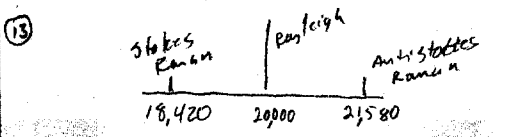
11 a) This does work out



The phase space plots show us the likelihood of a given position and momentum. We see that for higher T, more positions and momenta have high probabilities of being seen.



Superfluidity and superconductivity occur at low temps.



14 a) $v^M = \begin{bmatrix} 32 \\ 18 \\ 52 \\ 38 \end{bmatrix} \quad v^S = \begin{bmatrix} 102 \\ 56 \\ 102 \\ 120 \end{bmatrix}$

b)

| | | | |
|----|----|----|----|
| AA | AB | AC | AD |
| BA | BB | BC | BD |
| CA | CB | CC | CD |
| DA | DB | DC | DD |
| 3 | 2 | 3 | 4 |

c) $Tr[M] = 4 = W \checkmark \quad Tr[M^2] = 12 = W \checkmark$

d) $\frac{z}{N} = \frac{k_B h \nu}{N} = k_B h \lambda_{max} \quad \lambda_{max} = 3.17$
 $\frac{z}{N} = k_B h 3.17 = 1.453 k$

e) $Tr[M^4] = 104 \quad \frac{z}{N} = \frac{k_B h \nu}{N} 104 = 1.161 k$
 $\frac{1.161 - 1.153}{1.161} = 0.68\%$ error

15 a) $v_1 = \begin{bmatrix} 1 \\ 2 \\ 3 \\ 1 \end{bmatrix} \quad v_2 = \begin{bmatrix} 1 \\ 3 \\ 6 \\ 10 \end{bmatrix} \quad v_3 = \begin{bmatrix} 1 \\ 4 \\ 10 \\ 20 \end{bmatrix} \quad v_4 = \begin{bmatrix} 1 \\ 5 \\ 15 \\ 35 \end{bmatrix}$

b)

| | | | |
|-----|-----|-----|------|
| AAA | AAB | AAC | AAD |
| 1 ✓ | ABB | ABC | ABD |
| | BBB | BCB | ACD |
| | 3 ✓ | BCC | AOD |
| | | CCB | BBD |
| | | 6 ✓ | BCD |
| | | | 6 ✓ |
| | | | 10 ✓ |

c) $\frac{z}{N} = k_B h \nu \lambda_{max}, \quad \lambda_{max} = 1 \quad \frac{z}{N} = k_B h \nu = 0$
 As $N \rightarrow \infty$ change that and with an infinite number of D's over which all else.