CHM 8309: Statistical Mechanics / Saman Alavi / University of Ottawa

Problem Set – Due Oct. X, 2022

Please hand in Excel spreadsheets as supporting documents (via email), but present your answers in a Word or PDF document. Cut and paste the graphs from Excel into the Word document when needed.

1) (40 points) a) A mass of 1 kg is connected to a spring with force constant of 1 kg/s^2 and a natural length of 30 cm. The mass is constrained to move in one dimension. In one experiment, the mass is pulled such that the spring is extended by 5 cm and then released. In a second experiment, the mass is pulled such that the spring is extended by 12 cm and then released.

Plot the two phase space trajectories for these cases on the same graph and indicate the starting point of the motion along with the direction of motion in each trajectory.

b) If a point in the phase space of the harmonic oscillator is given, how would we determine the corresponding phase space trajectory?

For this problem, use Excel or computer coding for numerical calculations. Calculations by hand will be too time consuming! If you are not familiar with numerical calculations in Excel a small tutorial can be arranged.

2) (40 points) The energy levels of N non-interacting molecules in a quantum mechanical box are given by,

$$E_N = \sum_{\nu=1}^{N} \varepsilon_\nu (V) = \frac{h^2}{8mV^{2/3}} \sum_{\nu=1}^{N} \left(n_{x\nu}^2 + n_{y\nu}^2 + n_{z\nu}^2 \right)$$

a) For a system with 1 molecule, what are the six lowest energy levels? Write the energy levels in unit-less form as multiples of $a = h^2/8mV^{2/3}$. Determine the degeneracy of each energy level.

b) For a system with the same volume as part a) with two molecules, what are the six lowest energy levels? Write the energy levels in unit-less form as $8mV^{2/3}E/h^2$. Determine the degeneracy of each energy level.

c) If the volume of a box with one molecule increases such that $V_{new} = 1.5V_{old}$, what are the energies of the six lowest levels of the system.

Describe how the energy levels of a system change when the number of molecules increases and the volume of the system changes.

d) Consider an individual krypton atom as part of an ideal gas in a cubic box of macroscopic size of 10 cm on a side. What is the gap between the first two energy levels for a single Kr atom in a box of this size? Compare this energy with the magnitude of the average kinetic energy of an krypton atom at 300 K which is $3kT/2$.

3) (20 points) The Gaussian distribution

Consider two Gaussian functions: One with ($x_0 = 3$; $\sigma = 2$) and the second with ($x_0 = -1$; $\sigma = 3$).
a) Plot the individual Gaussian functions and their product, for example, with Excel. Visually show that the product of the two Gaussian functions is also a Gaussian function.

b) What is the x_0 value for the product Gaussian function (you can read it off the graph)? How does the standard deviation of the product function compare to the individual Gaussians?

4) (20 points) Consider a system of non-interacting molecules each having equally spaced energy levels (similar to that discussed in the lectures).

a) For a case with six molecules in this system with a total energy of $E_{\mathrm{tot}} = 6$, determine all possible distributions for this case and the degeneracy of each distribution. Plot the probabilities of occupancy of each of the levels 0, 1, …, 6 in this system over the entire ensemble of systems.

b) Consider a system with 6 molecules, but a total energy of $E_{\mathrm{tot}} = 9$. Repeat the above exercise. How do the probabilities of occupancies of different levels change in this case?

5) (40 points) Maxwell distribution

a) Plot the distribution function for the energy of one molecule in an ideal gas (E_1), for the sum of the energies of two molecules of an ideal gas (E_2), and for the sum energies of 4 molecules of an ideal gas system (E_4) on the same graph in terms of the variable of E/kT. For each distribution function, show the most probable energy E_P and the average value of the energy $\langle E \rangle$ on the graph.

b) Replot the three distribution functions mentioned above as a function of the reduced energy $E^* = E/E_P$. How do the standard deviations (widths) of these three distribution functions change as a function of the reduced energy E^*.

c) For each distribution, calculate or graphically determine the probability of observing an energy value twice the most probable energy, i.e., determine $P(E_{2P})$ and compare it to $P(E_P)$.

Explain why it becomes less probable to have an energy twice the most probable energy as the number of molecules in the system increases.

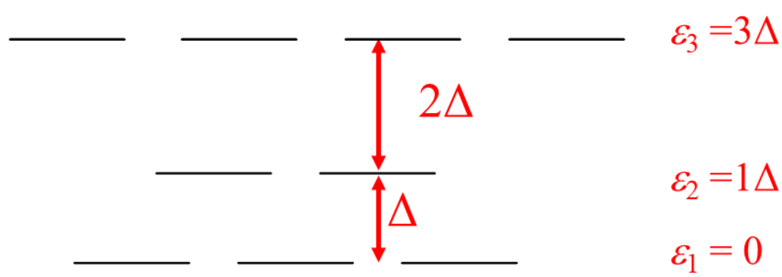
6) (20 points) Lagrange Multipliers

(a) Find the maximum / minimum of the function $f(x,y) = x^2 + y^2$ subject to the constraint that $g(x,y) = 2x + y - 5 = 0$. Determine the gradients of these two functions at the maximum point.

(b) Find the maxima and minima of a function, $f(x,y) = x^2y$ subject to the constraint that $g(x,y) = x^2 + y^2 - 1 = 0$

7) (30 points) The canonical partition function for a one molecule system.

Independent molecules in a system have quantum states with the energy level structure shown below. The system has nine states and three energy levels which are spaced with an energy gap of Δ in between them.



a) Plot the partition function and probability of observing the three energy levels as a function of temperature. Express the temperature in units of Δ/k. Go up to a temperature of $15k/\Delta$.

b) Plot the average energy, the variance in energy, and heat capacity for the system from temperature 0 up to $15k/\Delta$. Interpret the behavior of these graphs.

c) Plot the entropy of the system from temperature 0 up to $15k/\Delta$. Interpret the temperature behaviour of the entropy.