

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

Problem Set – Due Oct. 7, 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  $1 \text{ kg/s}^2$  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.

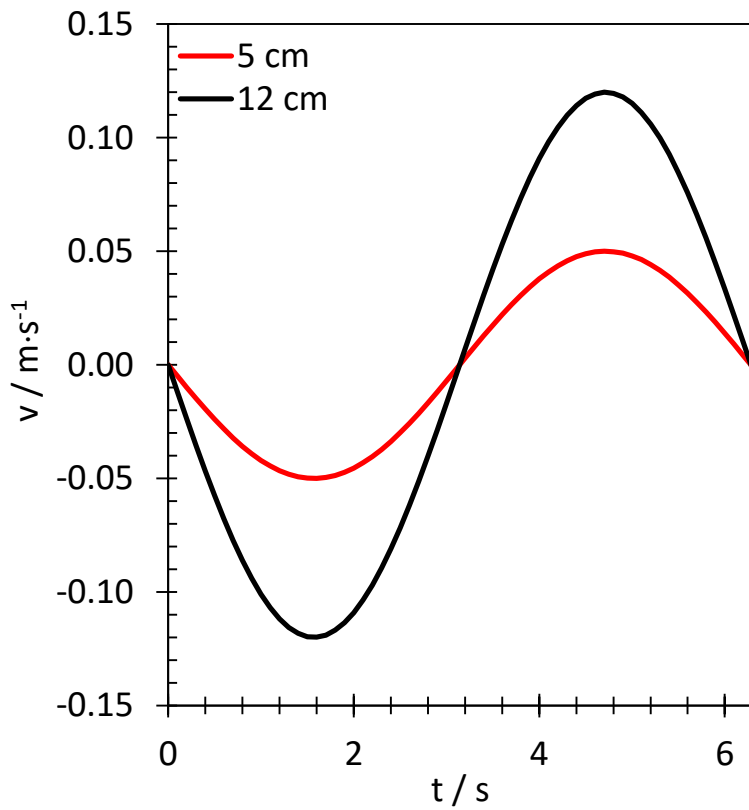
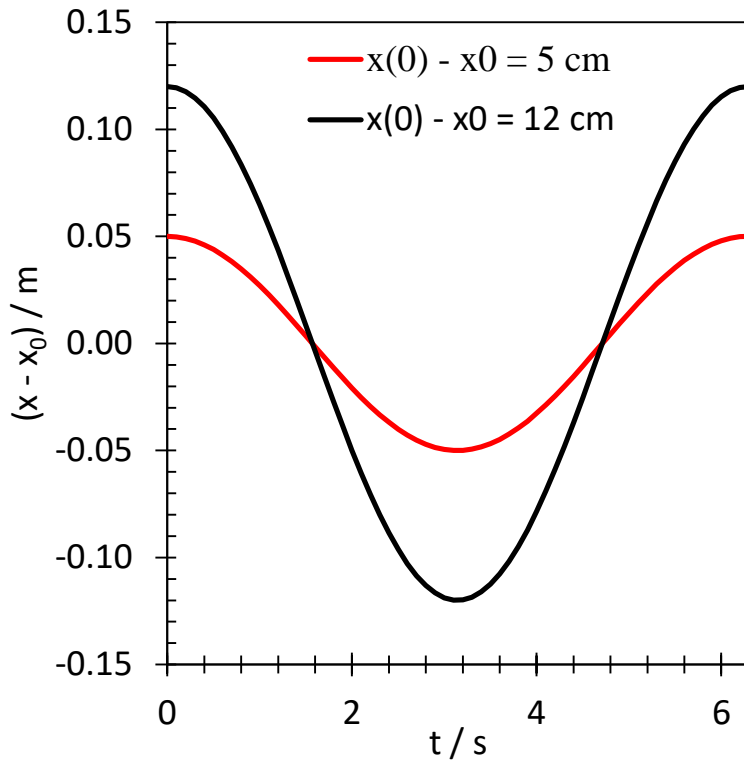
Plot the two phase space trajectories for these cases on the same graph and indicate the starting point of the motion along with the direction of motion in each trajectory.

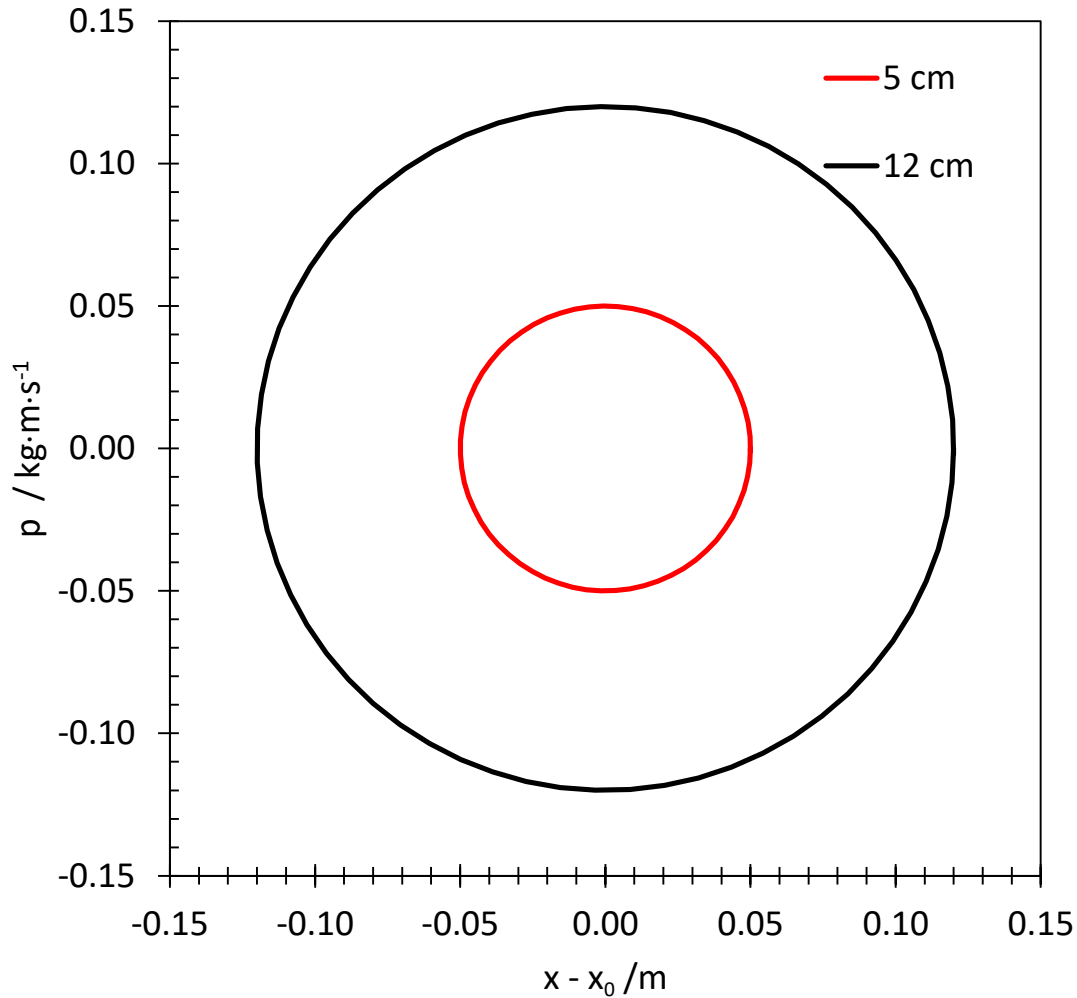
$$\xi = 0.05 \text{ m} \rightarrow E = 0.5 \times k \times \xi^2 = 0.5 \times 1 \times (0.05)^2 = 1.25 \times 10^{-3} \text{ kg}\cdot\text{m/s}^2 = 1.25 \times 10^{-3} \text{ J}$$

$$E = 0.5 \times m \times v_{max}^2 \rightarrow v_{max} = (2.5 \times 10^{-3})^{1/2} = 0.05 \text{ m/s}$$

$$\xi = 0.12 \text{ m} \rightarrow E = 0.5 \times k \times \xi^2 = 0.5 \times 1 \times (0.12)^2 = 7.2 \times 10^{-3} \text{ kg}\cdot\text{m/s}^2 = 7.2 \times 10^{-3} \text{ J}$$

$$E = 0.5 \times m \times v_{max}^2 \rightarrow v_{max} = (1.0 \times 10^{-2})^{1/2} = 0.12 \text{ m/s}$$





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

Substitution in the equation for the trajectory and finding the constants of the motion corresponding to the specific energy.

$$p_{\xi}^2(t) + \frac{2mE_0}{A^2} \xi^2(t) = 1$$

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.

In terms of multiples of  $8mV^{2/3}E/h^2$  the (energies, degeneracies) of the levels are:

(3, 1), (6, 3), (9, 3), (11, 3), (12, 1), (14, 6)

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.

In terms of multiples of  $8mV^{2/3}E/h^2$  the (energies, degeneracies) of the levels are:

(6, 1), (9, 6), (12, 15), (14, 6), (15, 20)

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.

For  $V_{new} = 1.5V_{old}$  we have  $E_{new} = E_{old}/(1.5)^{2/3} = 0.76E_{old}$ . All the energies in part (a) would be multiplied by 0.76.

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

The energy levels are more closely spaced in the system with larger volume.

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  $3kT/2$ .

	1 nm	1 cm	Description
M / g/mol	83.80	83.80	Atomic mass of krypton
Mass of Kr / kg	$1.3916 \times 10^{-25}$	$1.3916 \times 10^{-25}$	Mass of Kr in grams
V / m <sup>3</sup>	1.0000E-27	1.0000E-06	Volume of the system
h / (m <sup>2</sup> *kg/s)	$6.6260 \times 10^{-34}$	$6.6260 \times 10^{-34}$	Planck's constant
N_A	$6.0220 \times 10^{23}$	$6.0220 \times 10^{23}$	Avogadro's number
$h^2/8mV^{2/3}$	$3.9438 \times 10^{-25}$	$3.9438 \times 10^{-39}$	(m <sup>4</sup> kg <sup>2</sup> /s <sup>2</sup> )/(kg·m <sup>2</sup> )
k / (m <sup>2</sup> kg/s <sup>2</sup> K)	$1.3810 \times 10^{-23}$	$1.3810 \times 10^{-23}$	Boltzmann's constant

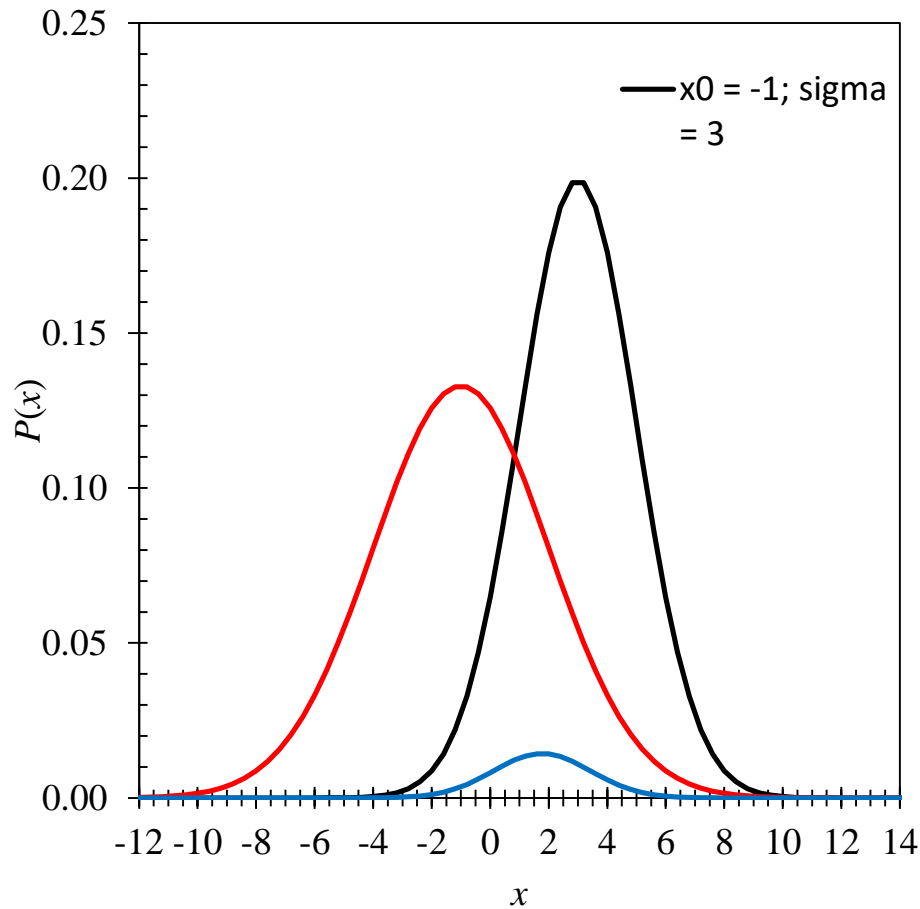
T / K	300	300	
$1.5kT / \text{kgm}^2/\text{s}^2$	$6.21 \times 10^{-21}$	$6.21 \times 10^{-21}$	Average thermal energy
$\Delta E / (1.5kT)$	$1.9038 \times 10^{-4}$	$1.9038 \times 10^{-18}$	

See the table for a calculation of the energy level for the particle in a box along with the thermal energy at 300 K. The gap between energy levels for a cubic box of 10 cm length is smaller by a factor of  $10^{-18}$  than the thermal energy.

### 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?

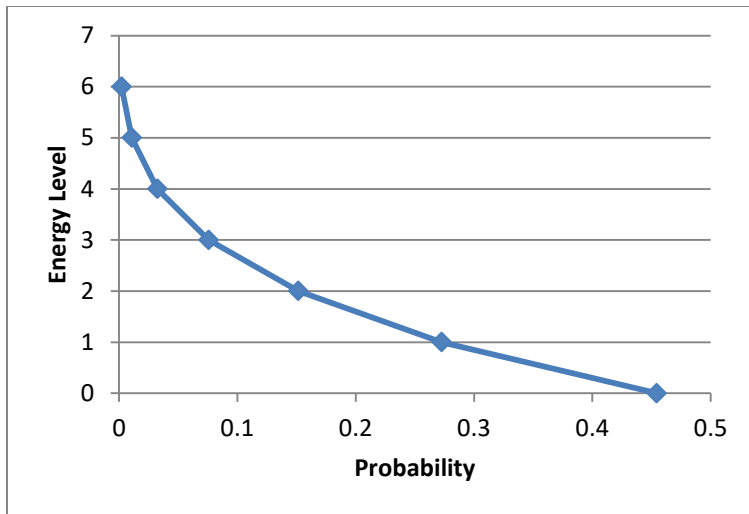
$x_0$  for the product function is around 1.6. Notice the product is not normalized. The product distribution looks narrower than the two distributions used in the convolution.

**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  $E_{\text{tot}} = 6$ , 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.

The eleven possible distributions among the levels with energy of 0 to 6, the number of ways to determine each distribution are shown in the table below. The probability of each level being occupied among all distributions is plotted below, showing a graded overall distribution of states.

d	0	1	2	3	4	5	6	w	n	Total
<b>1</b>	0	6	0	0	0	0	0	1	6	6
<b>2</b>	1	4	1	0	0	0	0	30	6	6
<b>3</b>	2	3	0	1	0	0	0	60	6	6
<b>4</b>	2	2	2	0	0	0	0	90	6	6
<b>5</b>	3	2	0	0	1	0	0	60	6	6
<b>6</b>	3	1	1	1	0	0	0	120	6	6
<b>7</b>	3	0	3	0	0	0	0	20	6	6
<b>8</b>	4	1	0	0	0	1	0	30	6	6
<b>9</b>	4	0	1	0	1	0	0	30	6	6
<b>10</b>	4	0	0	2	0	0	0	15	6	6
<b>11</b>	5	0	0	0	0	0	1	6	6	6



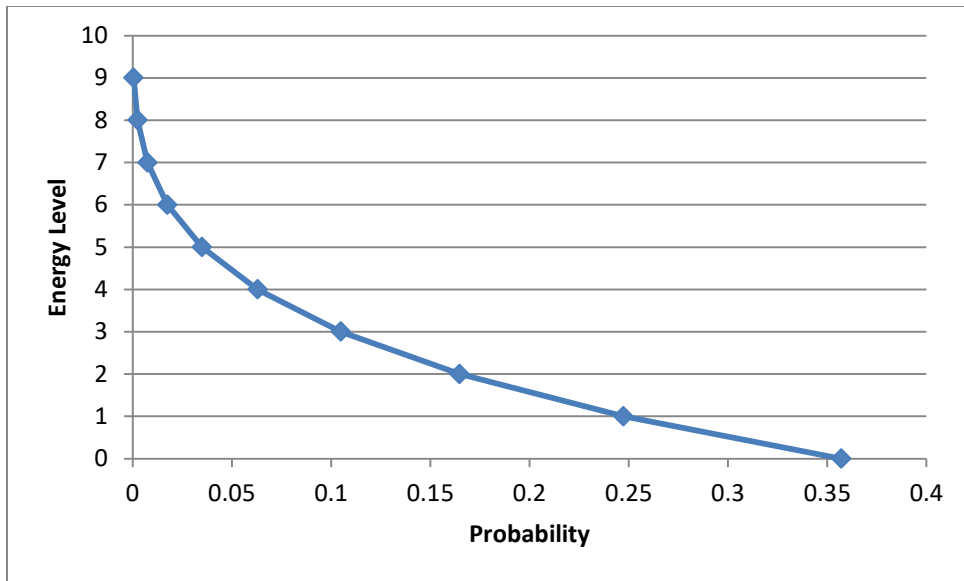
b) Consider a system with 6 molecules, but a total energy of  $E_{\text{tot}} = 9$ . Repeat the above exercise. How do the probabilities of occupancies of different levels change in this case?

The 25 distributions among the levels with energy of 0 to 9, the number of ways to determine each distribution are shown in the table below. The probability of each level being occupied is plotted below, showing a graded overall distribution of states.

d	0	1	2	3	4	5	6	7	8	9	w	n	Total
1	5	0	0	0	0	0	0	0	0	1	6	6	9
2	4	1	0	0	0	0	0	0	1	0	30	6	9
3	4	0	1	0	0	0	0	1	0	0	30	6	9
4	4	0	0	1	0	0	1	0	0	0	30	6	9
5	4	0	0	0	1	1	0	0	0	0	30	6	9
6	3	2	0	0	0	0	0	1	0	0	60	6	9
7	3	1	1	0	0	0	1	0	0	0	120	6	9
8	3	1	0	0	2	0	0	0	0	0	60	6	9

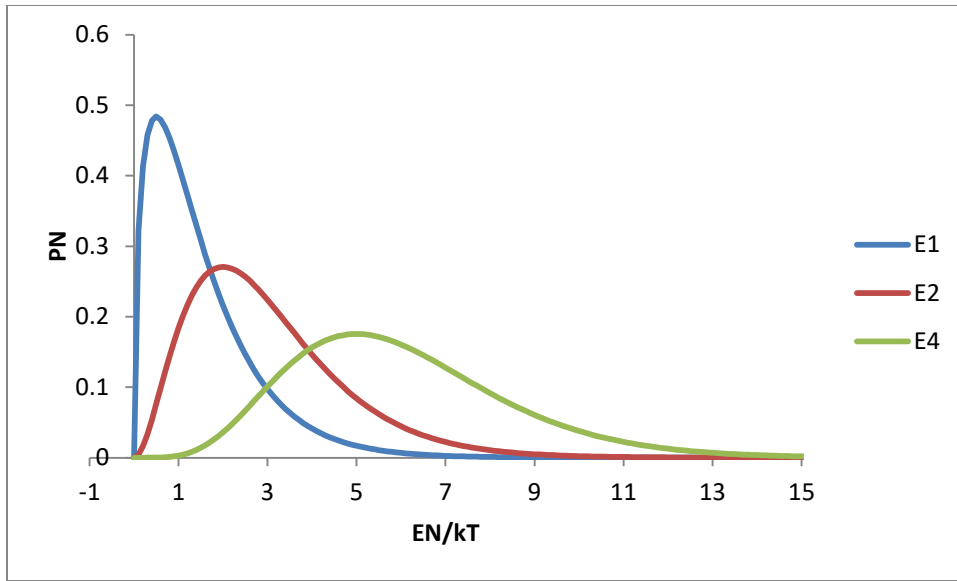


<b>9</b>	3	1	0	1	0	1	0	0	0	0	120	6	9
<b>10</b>	3	0	1	1	1	0	0	0	0	0	120	6	9
<b>11</b>	3	0	2	0	0	1	0	0	0	0	60	6	9
<b>12</b>	3	0	0	3	0	0	0	0	0	0	20	6	9
<b>13</b>	2	3	0	0	0	0	1	0	0	0	60	6	9
<b>14</b>	2	2	1	0	0	1	0	0	0	0	180	6	9
<b>26</b>	2	2	0	1	1	0	0	0	0	0	180	6	9
<b>15</b>	2	1	2	0	1	0	0	0	0	0	180	6	9
<b>16</b>	2	1	1	2	0	0	0	0	0	0	180	6	9
<b>17</b>	2	0	3	1	0	0	0	0	0	0	60	6	9
<b>18</b>	1	4	0	0	0	1	0	0	0	0	30	6	9
<b>19</b>	1	3	1	0	1	0	0	0	0	0	120	6	9
<b>20</b>	1	3	0	2	0	0	0	0	0	0	60	6	9
<b>21</b>	1	2	2	1	0	0	0	0	0	0	180	6	9
<b>22</b>	1	1	4	0	0	0	0	0	0	0	30	6	9
<b>23</b>	0	5	0	0	1	0	0	0	0	0	6	6	9
<b>24</b>	0	4	1	1	0	0	0	0	0	0	30	6	9
<b>25</b>	0	3	3	0	0	0	0	0	0	0	20	6	9
<b><math>P_i</math></b>	0.357143	0.247253	0.164835	0.104895	0.062937	0.034965	0.017483	0.007493	0.002498	0.0005	2002		



**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.

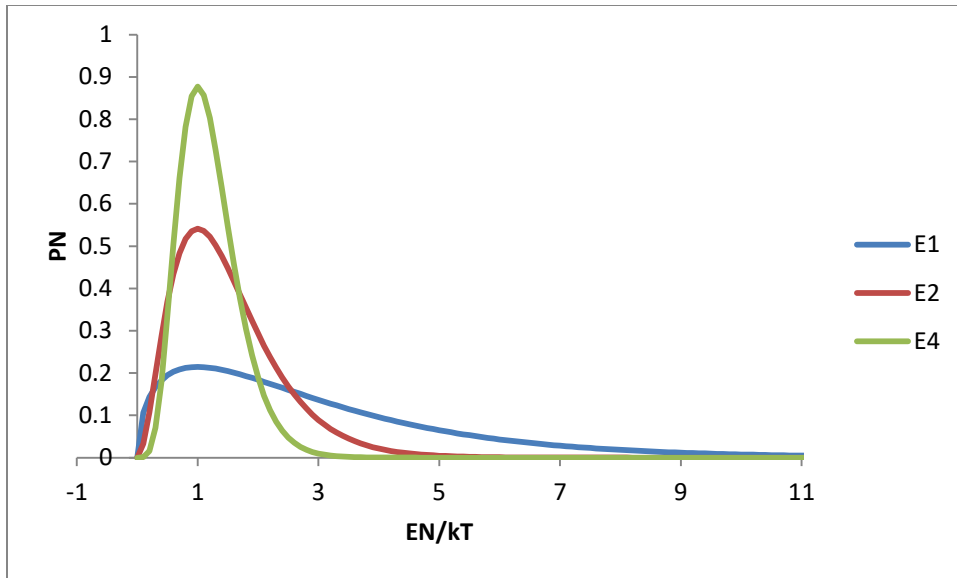


$P_1(E): E_P = kT/2 ; \langle E \rangle = 3kT/2$

$P_2(E): E_P = 2kT ; \langle E \rangle = 3kT$

$P_4(E): E_P = 5kT ; \langle E \rangle = 6kT$

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  $E^*$ .



The width of the distribution is seen become more narrow as the number  $N$  increases.

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.

For the distributions in part (a), the calculations in the attached spreadsheet show:

$$P_1(kT/2) = 0.47837; \quad P_1(kT) = 0.41511 \quad P_1(E_P)/P_1(E_{2P}) = 1.15$$

$$P_2(2kT) = 0.27067; \quad P_2(4kT) = 0.14652 \quad P_2(E_P)/P_2(E_{2P}) = 1.85$$

$$P_4(5kT) = 0.17547; \quad P_4(10kT) = 0.03783 \quad P_4(E_P)/P_4(E_{2P}) = 4.64$$

The increase in number of particles leads to a narrowing of the distribution and the trend in the  $P(E_P)/P(E_{2P})$  values. This may not be apparent from the figure in part (a).

## 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.

$$f(x, y) = x^2 + y^2 \text{ and } g(x, y) = 2x + y - 5 = 0$$

$$\Lambda(x, y, \lambda) = f(x, y) - \lambda g(x, y) = x^2 + y^2 - \lambda(2x + y - 5)$$

$$\begin{cases} \frac{d\Lambda(x, y, \lambda)}{dx} = 2x - 2\lambda = 0 \\ \frac{d\Lambda(x, y, \lambda)}{dy} = 2y - \lambda = 0 \\ \frac{d\Lambda(x, y, \lambda)}{d\lambda} = -(2x + y - 5) = 0 \end{cases}$$

Substituting for x and y in terms of  $\lambda$  in the last equation gives  $(2\lambda + \lambda/2 - 5) = 0$

$$(\lambda, x, y) = (2, 2, 1)$$

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

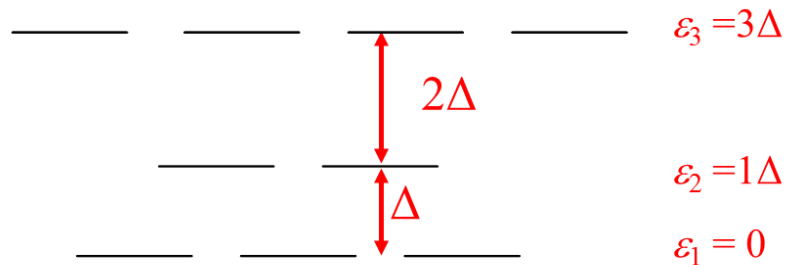
$$\begin{cases} \frac{d\Lambda(x, y, \lambda)}{dx} = 2xy - 2x\lambda = 0 \\ \frac{d\Lambda(x, y, \lambda)}{dy} = x^2 - 2y\lambda = 0 \\ \frac{d\Lambda(x, y, \lambda)}{d\lambda} = -(x^2 + y^2 - 1) = 0 \end{cases}$$

Substituting for x and y in terms of  $\lambda$  in the last equation gives  $(2\lambda^2 + \lambda^2 - 1) = 0$

$$(\lambda, x, y) = (1/\sqrt{3}, \pm 2/\sqrt{3}, 1/\sqrt{3}); (\lambda, x, y) = (-1/\sqrt{3}, \pm 2/\sqrt{3}, -1/\sqrt{3})$$

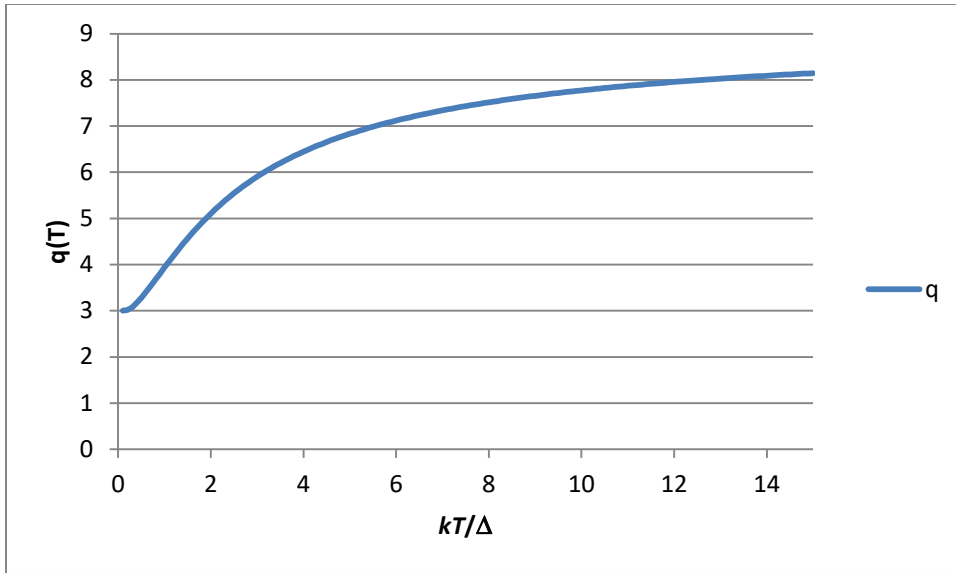
7) (30 points) The canonical partition function for a one molecule system.

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  $\Delta$  in between them.

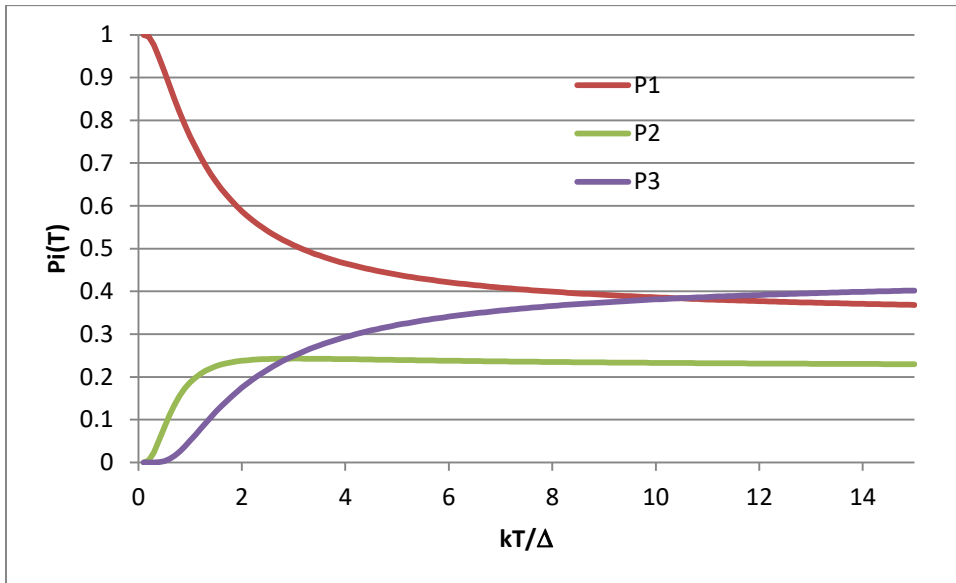


a) Plot the partition function and probability of observing the three energy levels as a function of temperature. Express the temperature in units of  $\Delta/k$ . Go up to a temperature of  $15k/\Delta$ .

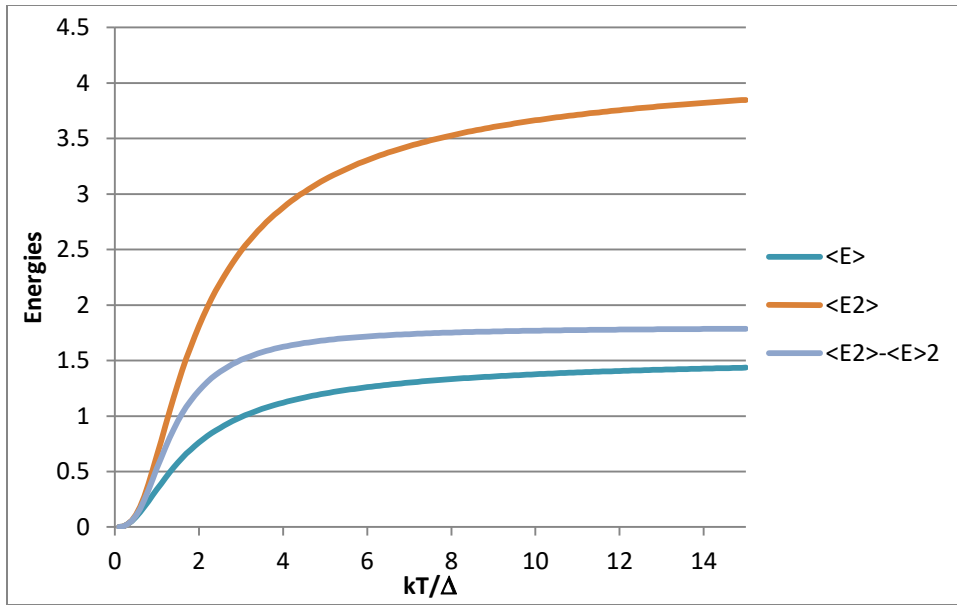
Plot of the temperature dependence of the partition function



Plot of the temperature dependence of the probabilities of occupancy of the three states

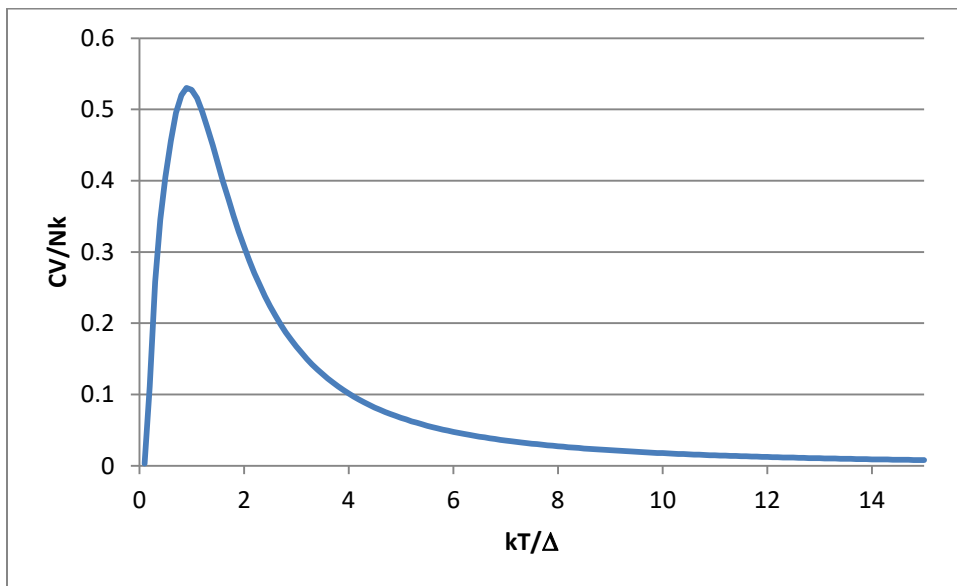


b) Plot the average energy, the variance in energy, and heat capacity for the system from temperature 0 up to  $15k/\Delta$ . Interpret the behavior of these graphs.



The average energy at high temperature goes to  $(3 \times 0 + 2 \times 1 + 4 \times 3) / 9 = 14 / 9 = 1.56$ . At high temperatures, the  $\langle E \rangle$  and  $\langle E^2 \rangle$  are close to their asymptotic values and so the variance is somewhat constant.

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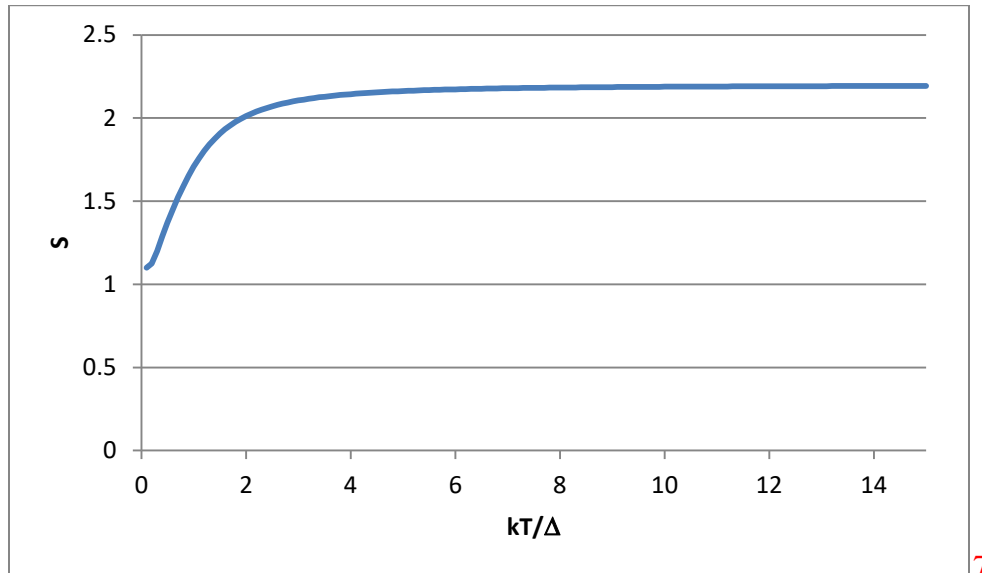


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-The maximum in  $C_V$  occurs when the thermal energy becomes equal to the energy gaps and the system can be excited to higher levels. The system then has the highest capacity to adsorb energy.

-Because there are a limited number of energy states, the  $C_V$  ultimately becomes zero when the levels are saturated and no more energy can be adsorbed. 5

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



The initial rise is due to increasing “disorder” in the system. As more energy becomes available to the system, more ways of distributing the energy among a number of different energy levels can be found. As temperature increases and the energy levels become saturated, the entropy becomes constant. 3