

Problem 1. Manipulating Taylor series

You are expected to know the following Taylor series in addition to $\sin(x)$ and $\cos(x)$:

$$e^x = 1 + x + \frac{1}{2!}x^2 + \mathcal{O}(x^3) \quad (1)$$

$$\log(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \mathcal{O}(x^4) \quad (2)$$

$$(1+x)^\alpha = 1 + \alpha x + \frac{\alpha(\alpha-1)}{2!}x^2 + \frac{\alpha(\alpha-1)(\alpha-2)}{3!}x^3 + \mathcal{O}(x^4) \quad (3)$$

$$\frac{1}{1+x} = 1 - x + x^2 + \mathcal{O}(x^3) \quad (4)$$

These get me through life. Here x is considered to be a small, dimensionless, number. The $\mathcal{O}(x^3)$ etc shows an estimate for the size of the terms that have been dropped. Some Taylor expansions will be needed in the next problem and throughout the course. These are to be found by combining the Taylor series above.

- (a) (Optional) Show that Eq. (2) follows from Eq. (4) by integration.
- (b) (Optional) Show that the Taylor series $(1+x)^\alpha$ gives the exact result for $\alpha = 2$.
- (c) Consider large x , i.e. $x \gg 1$. Then e^{-x} is very small, i.e. $e^{-x} \ll 1$. Show that

$$\frac{1}{e^x - 1} \simeq e^{-x} (1 + e^{-x} + e^{-2x} + \mathcal{O}(e^{-3x})) \quad (5)$$

The first two terms are compared to the full function in Fig. 1

- (d) By combining the expansion of $1/(1+x)$ and e^x derive the following expansion for $x \ll 1$:

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2} + \frac{1}{12}x + \mathcal{O}(x^2) \quad (6)$$

The first two terms are compared to the full function in Fig. 1

Hint: First expand e^x to second order inclusive (i.e. the error is $\mathcal{O}(x^3)$). Substitute this in Eq. (6) and pull out a factor of $\frac{1}{x}$. You should find that the resulting expression takes

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} \left(\frac{1}{1+u} \right) \quad (7)$$

where $u \simeq \frac{1}{2}x + \frac{x^2}{6}$. Then expand

$$\frac{1}{1+u} \simeq 1 - u + u^2 + \mathcal{O}(x^3) \quad (8)$$

When evaluating u^2 to an accuracy of $\mathcal{O}(x^3)$ you can (and should!) keep only the first term of $u(x) \simeq \frac{1}{2}x$:

$$u^2 + \mathcal{O}(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + \mathcal{O}(x^3) \simeq \left(\frac{1}{2}x\right)^2 + \mathcal{O}(x^3) \quad (9)$$

This is better (and less work) than evaluating the “exact” result:

$$u^2 + O(x^3) = \left(\frac{1}{2}x + \frac{1}{6}x^2\right)^2 + O(x^3) = \frac{1}{4}x^2 + \frac{1}{6}x^3 + \frac{1}{36}x^4 + O(x^3), \quad (10)$$

which is mathematically inconsistent, since other terms of order $O(x^3)$ have already been discarded. Indeed, there is no reason to keep the terms $\frac{1}{6}x^3$ and $\frac{1}{36}x^4$ after other terms of order $O(x^3)$ and $O(x^4)$ have been discarded.

- (e) Following the methodology of (c), determine an approximate series for

$$\frac{1}{e^{-x} + 1} \quad (11)$$

for $x \gg 1$. This is useful in describing the thermodynamics of metals.

- (f) Following the methodology of part (d), combine Taylor series to show that

$$\log(1 - e^{-x}) \simeq \log(x) - \frac{1}{2}x + \frac{x^2}{24} + O(x^3) \quad (12)$$

for $x \ll 1$. This is useful in entropy of ideal gas of photons.

- (g) (Optional) A clever student will notice that Eq. (12) follows from Eq. (6) via integration as in part(a). Give the details of this clever thought process.

Problem 2. Energy of the quantum harmonic oscillator

Recall from Homework 5 Problem 1 that the mean energy of a single classical harmonic oscillator interacting with the thermal environment is

$$\langle E \rangle = k_B T \quad (13)$$

Now we will compare this classical result to the quantum version of the harmonic oscillator. This builds on Homework 4 Problem 3 and Homework 5 problem 3.

Recall that the energy levels of the oscillator are $E_n = n\hbar\omega_0$, where we have shifted what we call zero energy to be ground state energy $n = 0$, while higher vibrational states have $n = 1, 2, \dots$

- Determine the average energy $\langle E \rangle$ of the quantum harmonic oscillator at temperature T or $\beta = 1/k_B T$, using the partition function. Express your result using β and $\hbar\omega_0$. You can check your result using the next item.
- How is the mean vibrational quantum number $\langle n \rangle$ related to $\langle E \rangle$? Plot the mean number of vibrational quanta $\langle n \rangle$ versus $k_B T / \hbar\omega_0$ for $k_B T / \hbar\omega_0 = 0 \dots 4$. Determine (from your graph) the temperature in units of $\hbar\omega_0$ where $\langle n \rangle = 1$. I find $T = 1.4427 \hbar\omega_0 / k_B$.

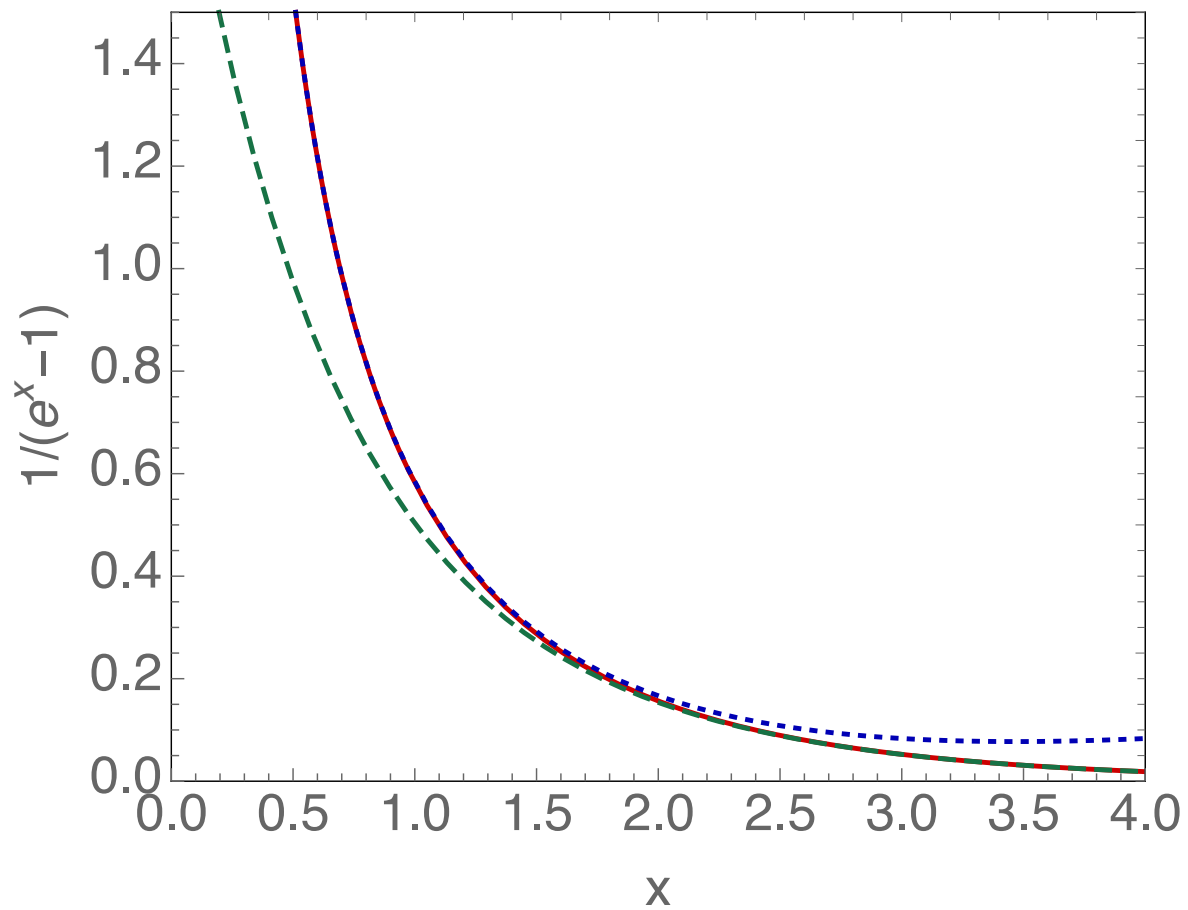


Figure 1: The function $1/(e^x - 1)$ (red) and our approximations to it. At small x the function is well approximated by $\frac{1}{x} - \frac{1}{2}$ (blue dotted line). At large x the function is well approximated by $e^{-x} + e^{-2x}$, green dashed line.

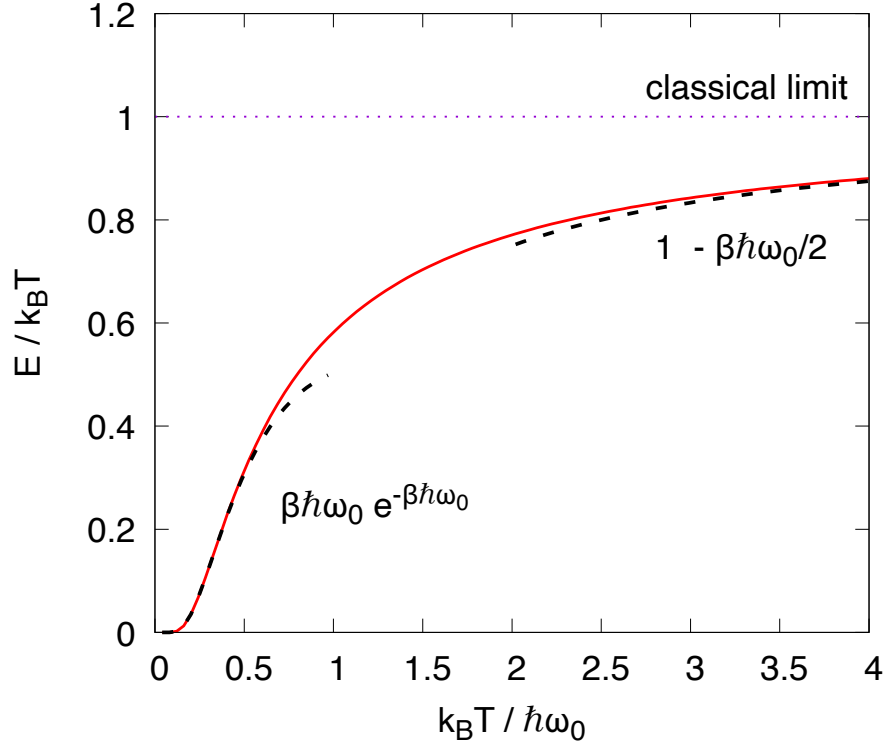


Figure 2: The energy $\langle E \rangle / k_B T$. Together with the expansions developed at large and small temperatures

(c) Plot

$$\frac{\langle E \rangle}{k_B T} \quad (14)$$

versus $k_B T / \hbar \omega_0$ for $k_B T / \hbar \omega_0 = 0 \dots 4$.

(d) You will now use the Taylor expansions of problem 2. Show that at low temperatures $T \ll \hbar \omega_0$ we have

$$\langle E \rangle \simeq \hbar \omega_0 e^{-\hbar \omega_0 / k_B T} \quad (15)$$

or more generally

$$\langle E \rangle \simeq \hbar \omega_0 e^{-\beta \hbar \omega_0} (1 + e^{-\beta \hbar \omega_0} + \dots) \quad (16)$$

Show that at high temperatures $T \gg \hbar \omega_0$ we have

$$\langle E \rangle \simeq k_B T \quad (17)$$

or more generally

$$\langle E \rangle \simeq k_B T \left(1 - \frac{\hbar \omega_0}{2 k_B T} + \dots \right) \quad (18)$$

A plot of the two approximations to the full function is shown in Fig. 2.

- (e) The high temperature limit $T \gg \hbar\omega_0$ is

$$\lim_{T \rightarrow \infty} \langle E \rangle \simeq k_B T \quad (19)$$

Explain why at high temperatures the $\langle E \rangle$ of the quantum oscillator agrees with the classical one by referring to the graph of (b).

- (f) Consider a diatomic gas. Recall that the mean energy of each molecule consists of a contribution from translational degrees of freedom $\frac{3}{2}k_B T$, a contribution from the rotational degrees of freedom $\frac{2}{2}k_B T$, and a contribution from the vibrational motion. The energy computed in part (a) is the contribution of vibrational motion, computed quantum mechanically. As discussed in class total energy takes the form

$$U = N f_0(T) \quad (20)$$

- (i) Determine $f_0(T)$ for the a diatomic molecule at temperature T .
(ii) Show that the specific heat C_p is

$$C_p = N k_B \left[\frac{7}{2} + \frac{(\beta \hbar \omega_0)^2 e^{-\beta \hbar \omega_0}}{(1 - e^{-\beta \hbar \omega_0})^2} \right] \quad (21)$$

and that the specific heat per mole

$$C_p^{1\text{ml}} = R \left[\frac{7}{2} + \frac{(\beta \hbar \omega_0)^2 e^{-\beta \hbar \omega_0}}{(1 - e^{-\beta \hbar \omega_0})^2} \right] \quad (22)$$

- (iii) Recall that for diatomic hydrogen the first vibrational frequency is¹ $\hbar\omega_0 \simeq 0.54 \text{ eV}$. Using this result together with $k_B = 0.025 \text{ eV}/300\text{K}$, I made a graph of Eq. (22) shown below. Compare the result to the experimental data. What qualitatively does the (simple-minded) calculation get right and wrong? Explain.

Problem 3. Blundell 14.5

- (a) Read and understand Example 14.1 from the text part of Blundell. (Nothing to turn in). The figure in Blundell is wrong (the entropy change of the universe doesn't go to zero). A corrected figure is shown in Fig. 4
- (b) Work problem 14.5 from Blundell.
- (c) (Optional) Work out the change in the entropy of the universe for Blundel 14.5

¹There was a 2π error in the previous homework. The inverse wavelength of the photon which excites the first level is $1/\lambda_0 = 4400 \text{ cm}^{-1}$. The homework said it was $k_0 = 2\pi/\lambda_0$. The confusion stems from a difference in terminology, see [here](#). The energy of the photon is $hc/\lambda = (1240 \text{ eV nm})(4400 \text{ cm}^{-1}) = 0.54 \text{ eV}$.

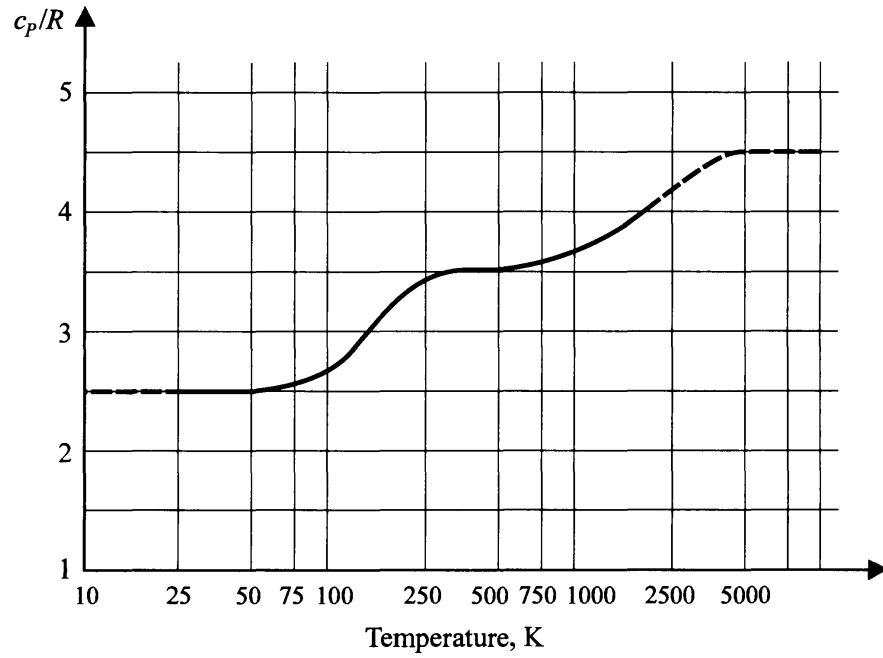
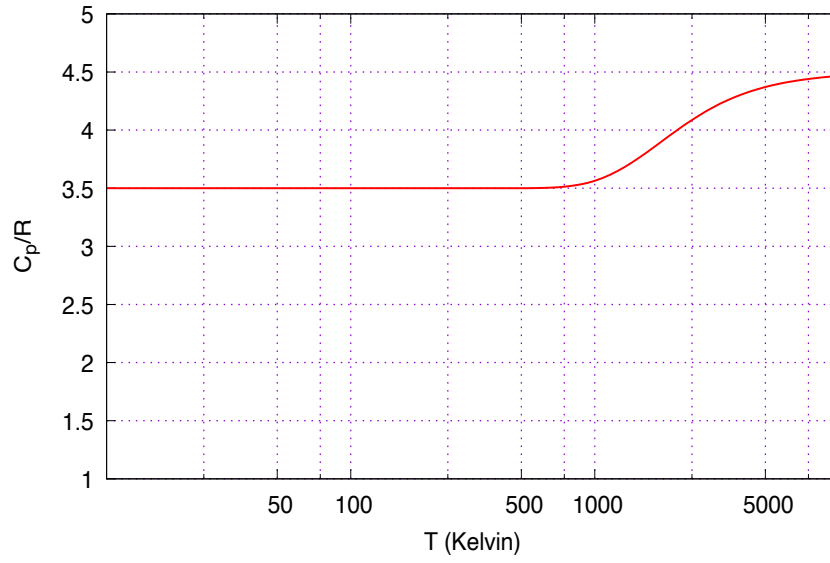


Figure 3: Top: a calculation of the specific heat per mole of diatomic hydrogen in units of R . Bottom: experimental data on C_p per mole in units of R

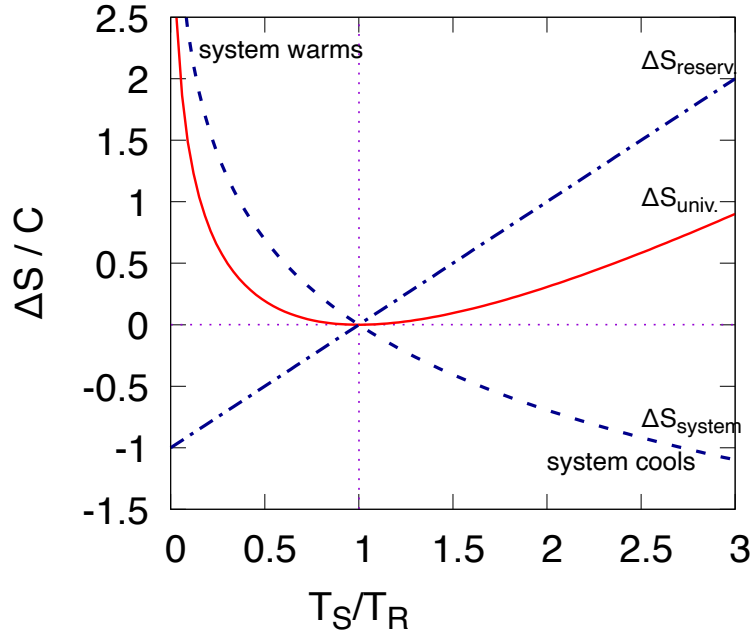


Figure 4: A graph of the change in entropy of the system ΔS_{system} (e.g. the ball thrown in the lake), the change in entropy of the reservoir $\Delta S_{\text{reservoir}}$ (e.g. the lake), and the universe $\Delta S_{\text{system}} + \Delta S_{\text{reservoir}}$.

Problem 4. Volume of Phase Space: Part II

The purpose is here to get started, talking about the accessible phase space volume. The phase space volume is a measure of the total number of possible ways for N of particles to *share* (or to partition) the total energy. For instance one particle could have almost all the available energy and the remaining $N-1$ could have very little. Those possible configurations of the particles occupy only a small portion of the available phase space volume.

- (a) Take two non-interacting particles in three dimensions sharing (or partitioning) the available energy which lies between E and $E + \delta E$

$$E < \frac{p_{x1}^2}{2m} + \frac{p_{y1}^2}{2m} + \frac{p_{z1}^2}{2m} + \frac{p_{x2}^2}{2m} + \frac{p_{y2}^2}{2m} + \frac{p_{z2}^2}{2m} < E + \delta E \quad (23)$$

The two particles can be anywhere in phase space, but the total energy must lie in this range. The coordinates are in a box $0 < x, y, z < L$. Show that the total phase space volume which is available to be shared amongst the six degrees of freedom $p_{x1}, p_{y1}, p_{z1}, p_{x2}, p_{y2}, p_{z2}$ is

$$V_{\text{ps}} = \int_{[E, E+\delta E]} d^3\mathbf{r}_1 d^3\mathbf{p}_1 d^3\mathbf{r}_2 d^3\mathbf{p}_2 = V^2 (2mE)^3 \pi^3 \frac{\delta E}{2E} \quad (24)$$

It is helpful to realize that the area of a sphere in six dimensions is given by a general formula

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} \quad (25)$$

So far we have been talking about phase space volume. Now we show how to translate the phase space volume into “the number of ways to share energy E ”, or in other words, the number of accessible configurations with energy between E and $E + \delta E$.

Lets go back to one particle in three dimensions which you worked out last week. Consider (again) a single particle in three dimensions in a box

$$0 < x, y, z < L \quad (26)$$

The three momenta components are sharing (or partitioning) the total energy which lies between E and $E + \delta E$, i.e.

$$E < \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} < E + \delta E, \quad (27)$$

The particle is free to move around in phase space but the energy must lie in this range. To count the number of configurations, divide up the phase space volume into cells of (arbitrary) small size $h_0 = \Delta x \Delta p_x$, or in three dimensions cells of size²

$$h_0^3 = (\Delta x \Delta y \Delta z) (\Delta p_x \Delta p_y \Delta p_z) \quad (28)$$

The “number of ways” for p_x , p_y , p_z and to share (or partition) the available energy is denoted by $\Omega(E)$ and it is phase space volume divided by the cell size

$$\Omega(E) = \frac{1}{h_0^3} \int_E^{E+\delta E} d^3\mathbf{r} d^3\mathbf{p} \quad (29)$$

$$= V \left(\frac{2mE}{h_0^2} \right)^{3/2} 4\pi \frac{\delta E}{2E} \quad (30)$$

$\Omega(E)$ is the number of accessible configurations for a single particle with energy between E and $E + \delta E$.

The number of accessible configurations for two particles sharing energy between E and $E + \delta E$ is

$$\Omega(E) = \frac{1}{2!} \int_E^{E+\delta E} \frac{d^3\mathbf{r}_1 d^3\mathbf{p}_1}{h_0^3} \frac{d^3\mathbf{r}_2 d^3\mathbf{p}_2}{h_0^3} \quad (31)$$

$$= V^2 \left(\frac{2mE}{h_0^2} \right)^3 \pi^3 \frac{\delta E}{4E} \quad (32)$$

The $2!$ is inserted because if I simply exchange what I call particle 1 and particle 2, that is not to be considered a new configuration.

- (b) (Optional: done in class) For two particles in one dimension what is the total number of accessible configurations $\Omega(E)$ with energy in range $[E, E + \delta E]$? This is visualized in Fig. 5.

²Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is the Plank constant h . But here lets understand it from a classical perspective first, choosing the cell size to be h_0 . We will drop the “0” eventually.

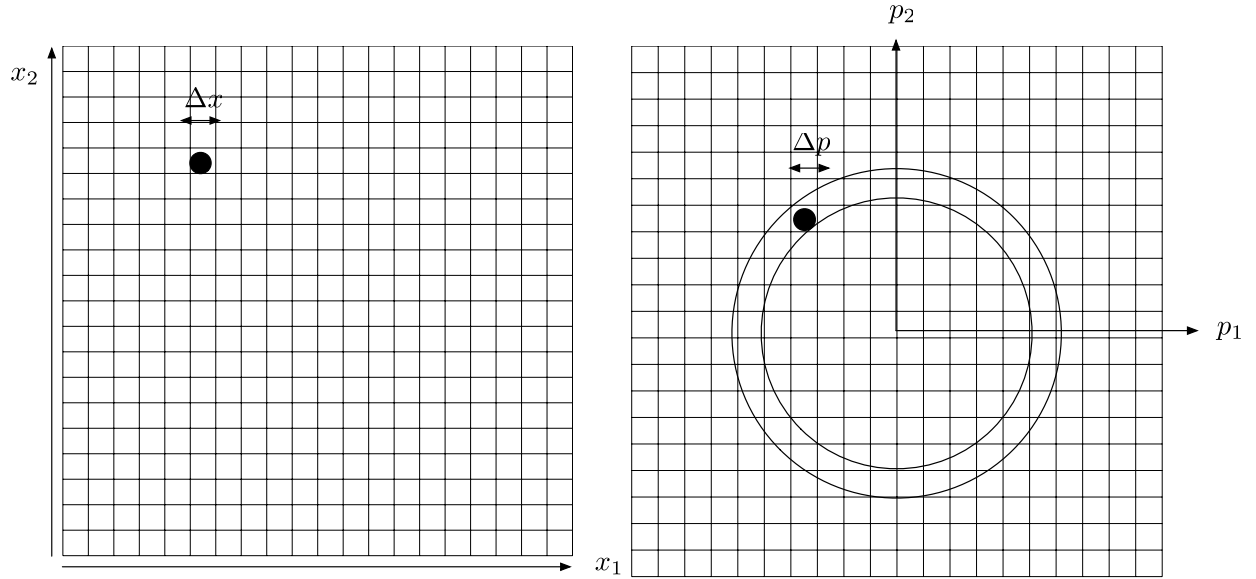


Figure 5: The available phase space for two particles in one dimension. The black points shows one possible configuration for (x_1, p_1, x_2, p_2) . The accessible phase space lies in a four dimensional space. One black point can be placed anywhere in the x_1, x_2 plane, and one black point can be placed in the grid somewhere in the shell in the p_1, p_2 plane, so that $2mE < p_1^2 + p_2^2 < 2m(E + \delta E)$. The cell size is $h_0 = \Delta x \Delta p$. The number of possible configurations is $\frac{1}{2!h_0^2} \int dx_1 dp_1 dx_2 dp_2$. For an Avogadro's number of particles in three dimensions, the space of accessible configurations is a $6N_A$ dimensional space.

- (c) Show that the total number of ways for N particles to share the energy E (i.e. total number of accessible configurations with energy E and $E + \delta E$) is

$$\Omega(E) = \frac{1}{N!} \int \frac{d^3\mathbf{r}_1 d^3\mathbf{p}_1}{h_0^3} \cdots \frac{d^3\mathbf{r}_N d^3\mathbf{p}_N}{h_0^3} = \frac{1}{N!} V^N \left(\frac{2\pi m E}{h_0^2} \right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E} \quad (33)$$

N here is like Avogadro's number large. (Just try and imagine how it depends on energy, e.g. what does the graph of x^{10} look like. Now what does $x^{10^{23}}$ look like.)

- (d) Use the Stirling approximation to show that³

$$\Omega(E) \simeq e^{5N/2} \left(\frac{V}{N} \right)^N \left(\frac{4\pi m E}{3h_0^2 N} \right)^{3N/2} \quad (34)$$

and that the entropy is

$$S = Nk_B \log \left[\left(\frac{V}{N} \right) \left(\frac{4\pi m E}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} Nk_B \quad (35)$$

$$= Nk_B \left[\log \left(\frac{v}{\lambda_{\text{th}}^3} \right) + \frac{5}{2} \right] \quad (36)$$

where $v = V/N = \ell_0^3$ is the volume per particle (see lecture 2), and

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}} \quad (37)$$

is the typical Debroglie wavelength (see lecture 2) at temperature T . Here T was taken from $E = \frac{3}{2} Nk_B T$. The result for S in Eq. (35) is known as the Sackur Tetrode equation.

Hint: for large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \quad (38)$$

Note the Stirling approximation works for n not integer, if $n!$ is understood as $\Gamma(n+1)$.

More Hints: The $\delta E/E$ term is not exponentially large (or small), in contrast to the other terms. Thus $\delta E/E$ can be set to one via the following approximations:

$$e^{5N/2} \left(\frac{\delta E}{E} \right) = e^{5N/2 + \log(\delta E/E)} \simeq e^{5N/2} \quad (39)$$

Convince yourself of this step by taking $\delta E/E = 10^{-6}$ (or whatever you like). How big is $\log(\delta E/E)$ compared to $5N/2$? Something is exponentially large if its logarithm is of order Avogadro's number.

³Forget about factors like $\sqrt{2\pi n}$ when evaluating $n!$. So $n! = (n/e)^n$, or $\log(n!) = n \log n - n$.