## Problem 1.   Flux in two dimensions

We are in two dimensions!

(a) First consder a beam of particles all with velocity v striking a hole head on (see figure). The density of particles in the beam is $n = N/A$. Determine the number of particles passing through the a hole of size ℓ per time. Explain how you arrived at the result. How would result change if the beam was incident at angle θ? Explain how you arrived at the result in this case. How would your result change in three dimensions?
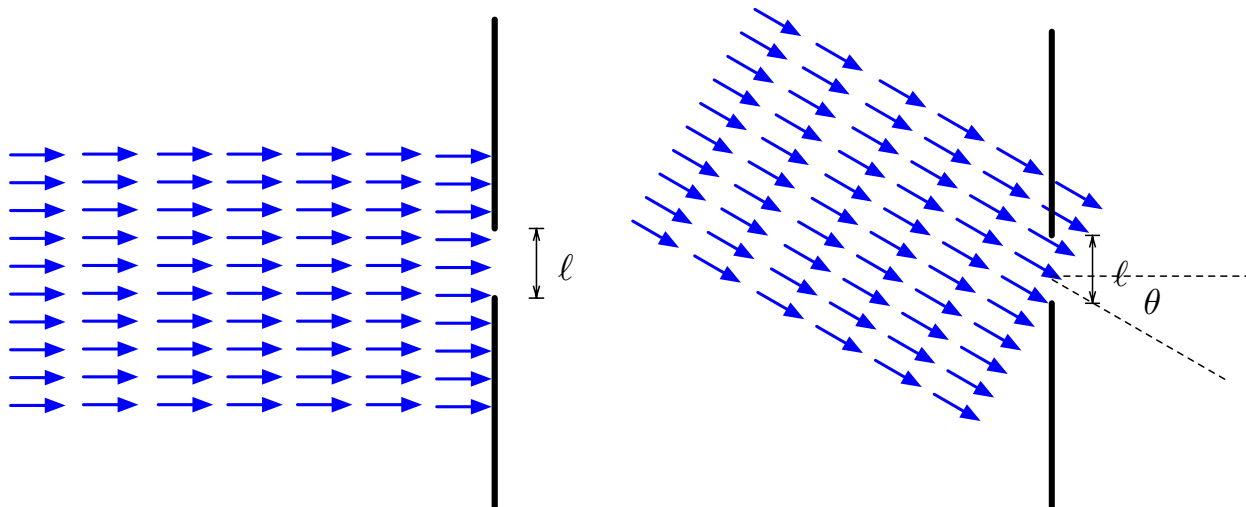
(b) Next consider a gas in two dimensions. Show that the density of particles with speed v in $[v, dv]$ and angle θ in $[\theta, d\theta]$ is

$$dn = nP(v)dv\frac{d\theta}{2\pi} \tag{1}$$

where $P(v)$ is the distribution of speeds. Determine[1] $P(v)$.

(c) A gas may be considered as a ensemble of beams with different speeds and incident angles. By integrating over these beams, show that passing the number of through a hole of length ℓ per time is

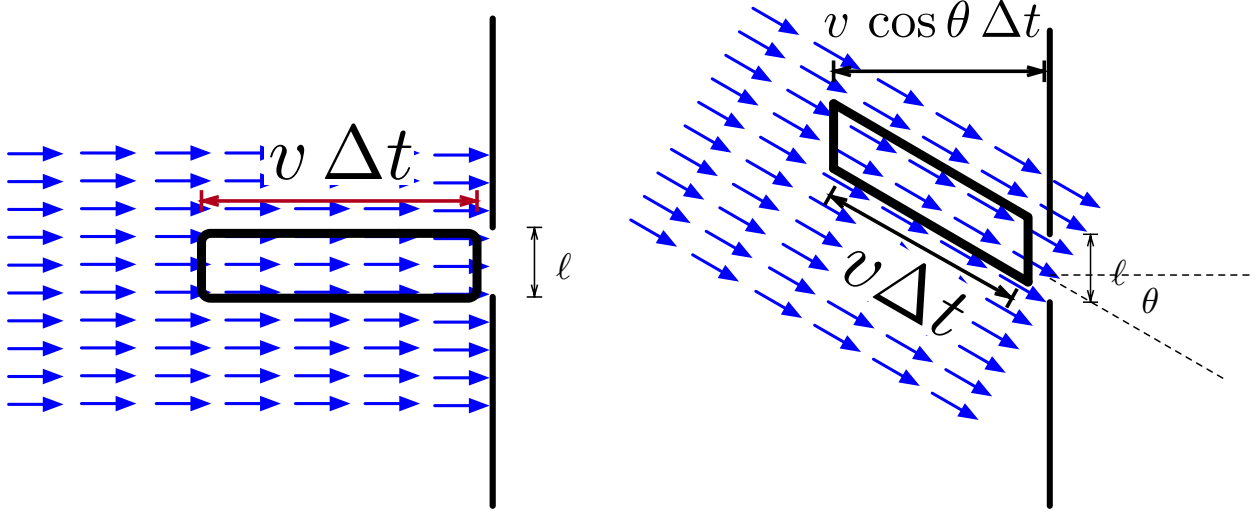$$\frac{dN}{dt} = \frac{1}{\pi}\ell n \langle v \rangle \tag{2}$$

where

$$\langle v \rangle = \sqrt{\frac{\pi}{2}\left(\frac{kT}{m}\right)} \tag{3}$$

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[1]You should find that $P(v)$ has no factors of π. You can also compute $\langle v \rangle$ and which is needed for the result below and given in Eq. (3).

Solution

(a) The "volume" of the gas passing through the hole in time Δt is $\ell v \Delta t$ (see figure).

Multiplying by the density, the number that pass through the hole is $n\ell v\Delta t$. So the number escaping per time is

$$\frac{dN_{esc}}{dt} = \ell n v \,. \tag{4}$$

When the beam "flies" at an angle θ, the volume is $\ell h = \ell v \cos\theta \Delta t$. So

$$\frac{dN_{esc}}{dt} = \ell n v \cos\theta \,. \tag{5}$$

(b) The probability to find a particle in $[v_x, \mathrm{d}v_x]$ and $[v_y, \mathrm{d}v_y]$ is

$$\mathrm{d}\mathscr{P} = \frac{m}{2\pi kT} e^{-mv^2/2kT}\, \mathrm{d}v_x \mathrm{d}v_y \,. \tag{6}$$

So writing in terms of speed and angles, we have by the change of variables discussed in pervious homework

$$d\mathscr{P}_{v,\theta} = \frac{m}{2\pi kT} e^{-mv^2/2kT} v \mathrm{d}v\,\mathrm{d}\theta \tag{7}$$

If we only care about the speed we can integrate over θ and find the speed distribution:

$$\mathrm{d}\mathscr{P}_v = \frac{m}{2\pi kT} e^{-mv^2/2kT} 2\pi v \mathrm{d}v \equiv P(v)\mathrm{d}v \tag{8}$$

Thus the probability density is

$$\frac{d\mathscr{P}}{dv} = P(v) = \frac{m}{kT} e^{-mv^2/2kT} v \tag{9}$$

So

$$d\mathscr{P}_{v,\theta} = P(v)\mathrm{d}v \frac{\mathrm{d}\theta}{2\pi} \tag{10}$$

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Multiplying by the number of particles per volume, we find the number per volume with $[v, \mathrm{d}v]$ and $[\theta, \mathrm{d}\theta]$ is

$$dn_{v,\theta} = nP(v)\mathrm{d}v\frac{\mathrm{d}\theta}{2\pi} \tag{11}$$

Or

$$\frac{dn}{\mathrm{d}v\,\mathrm{d}\theta} = \frac{1}{2\pi}nP(v) \tag{12}$$

(c) The gas can be thought of an ensemble of beams. Taking the density per speed and θ from (b) and using the result of parts (a), the number escaping per $\mathrm{d}v$ and $\mathrm{d}\theta]$ is

$$\frac{dN_{\mathrm{esc}}}{\mathrm{d}t\,\mathrm{d}v\,\mathrm{d}\theta} = \frac{1}{2\pi}nP(v)\ell v\cos\theta\,, \tag{13}$$

Integrating over the possible speeds and angles we have

$$\frac{dN_{\mathrm{esc}}}{\mathrm{d}t} = \frac{1}{2\pi}n\ell\int_0^\infty P(v)v\mathrm{d}v\int_{-\pi/2}^{\pi/2}\mathrm{d}\theta\cos\theta \tag{14}$$

$$= \frac{1}{2\pi}n\ell\langle v\rangle\times 2 \tag{15}$$

$$= \frac{1}{\pi}n\langle v\rangle\,. \tag{16}$$

We defined

$$\langle v\rangle = \int_0^\infty \frac{m}{kT}e^{-mv^2/2kT}v\cdot v\,\mathrm{d}v = \frac{m}{kT}\frac{1}{2}\sqrt{2\pi kT/m} = \sqrt{\frac{\pi}{2}\frac{kT}{m}}\,. \tag{17}$$

If you are confused by a factor of a half, note that we are integrating from 0 to ∞ and not $-\infty$ to ∞.

Problem 2. Manipulating Taylor Series Again

The function we will study in detail is wildly important:

$$\frac{1}{e^x - 1}. \tag{18}$$

It determines the average number of vibrational quanta in a quantum harmonic oscillator at temperature T.

(a) Consider large x, i.e. $x \gg 1$. Then $u \equiv e^{-x}$ is very small, i.e. $e^{-x} \ll 1$, and one may develop a Taylor series in u. Show that

$$\frac{1}{e^x - 1} \simeq e^{-x}\left(1 + e^{-x} + e^{-2x} + \mathcal{O}(e^{-3x})\right) \tag{19}$$

The first two terms are compared to the full function in Fig. 1. By examining the graph, estimate graphically at what x the approximation deviates from the full result at the 20% level.

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

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2} + \frac{1}{12}x + \mathcal{O}(x^2) \tag{20}$$

The first two terms are compared to the full function in Fig. 1 By examining the graph, estimate graphically at what x the approximation deviates from the full result at the 20% level.

(c) Following the methodology of (a), deduce the following series expansion for $\ln(1 + e^x)$

$$\ln(1 + e^x) \simeq x + e^{-x} - \frac{1}{2}e^{-2x} + \mathcal{O}(e^{-3x}) \tag{21}$$

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

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Manipulating Taylor Series

a) $\quad \dfrac{1}{1+x} = 1 - x + x^2 - x^3 + \ldots$

This follows from the geometric series
$1/(1-u) = 1 + u + u^2 + \ldots$ with $u = -x$

Integrating

$$\int_0^x \frac{dx'}{(1+x')} = \log(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} \ldots$$

b)

c) For x large we have $e^{-x} \ll 1$

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}}$$

call $\quad u = e^{-x} \ll 1$

$$\frac{1}{e^x - 1} = \frac{u}{(1-u)} = u(1 + u + u^2 + \ldots)$$

$$\boxed{\frac{1}{e^x - 1} = e^{-x}(1 + e^{-x} + e^{-2x} + O(e^{-3x}))}$$

d) $\dfrac{1}{e^x - 1}$

we expand $e^x = 1 + x + \dfrac{x^2}{2} + \dfrac{x^3}{6}$

$\dfrac{1}{e^x - 1} \simeq \dfrac{1}{x + x^2/2 + x^3/6} = \dfrac{1}{x} \; \dfrac{1}{(1 + x/2 + x^2/6 + O(x^3))}$

calling $u = x/2 + x^2/6$, we have

$\dfrac{1}{e^x - 1} \simeq \dfrac{1}{x} \left(\dfrac{1}{1 + u} + O(x^3) \right)$

$\simeq \dfrac{1}{x} \left(1 - u + u^2 + O(x^3) \right)$

$\simeq \dfrac{1}{x} \left(1 - \left(\dfrac{x}{2} + \dfrac{x^2}{6} \right) + \left(\dfrac{x^2}{4} \right) + O(x^3) \right)$

$\boxed{\dfrac{1}{e^x - 1} \simeq \dfrac{1}{x} \left(1 - \dfrac{x}{2} + \dfrac{x^2}{12} \right) + O(x^2)}$

e) $\dfrac{1}{e^{-x} + 1} \simeq 1 - e^{-x} + e^{-2x}$ \qquad set $u = e^{-x}$

f) $\log(1 - e^{-x}) \simeq \log \left(1 - \left(1 - x + \dfrac{x^2}{2} - \dfrac{x^3}{6} \right) \right)$

$\simeq \log x \left(1 - \dfrac{x}{2} + \dfrac{x^2}{6} \right) = \log x + \log \left(1 - \dfrac{x}{2} + \dfrac{x^2}{6} \right)$

So

$$\log(1 - e^{-x}) = \log(x) + \log \left(\underbrace{1 - \frac{x}{2} + \frac{x^2}{6}}_{\text{Call it } u} \right) + O(x^3)$$

Setting $u = -\frac{x}{2} + \frac{x^2}{6}$ we have

$$\log(1 + u) = u - \frac{u^2}{2} + O(u^3) \qquad \text{with} \qquad x \text{ of order } u$$

So

$$\log(1 - e^{-x}) = \log(x) + \left(-\frac{x}{2} + \frac{x^2}{6} \right) - \frac{1}{2} \left(-\frac{x}{2} \right)^2 + O(x^3)$$

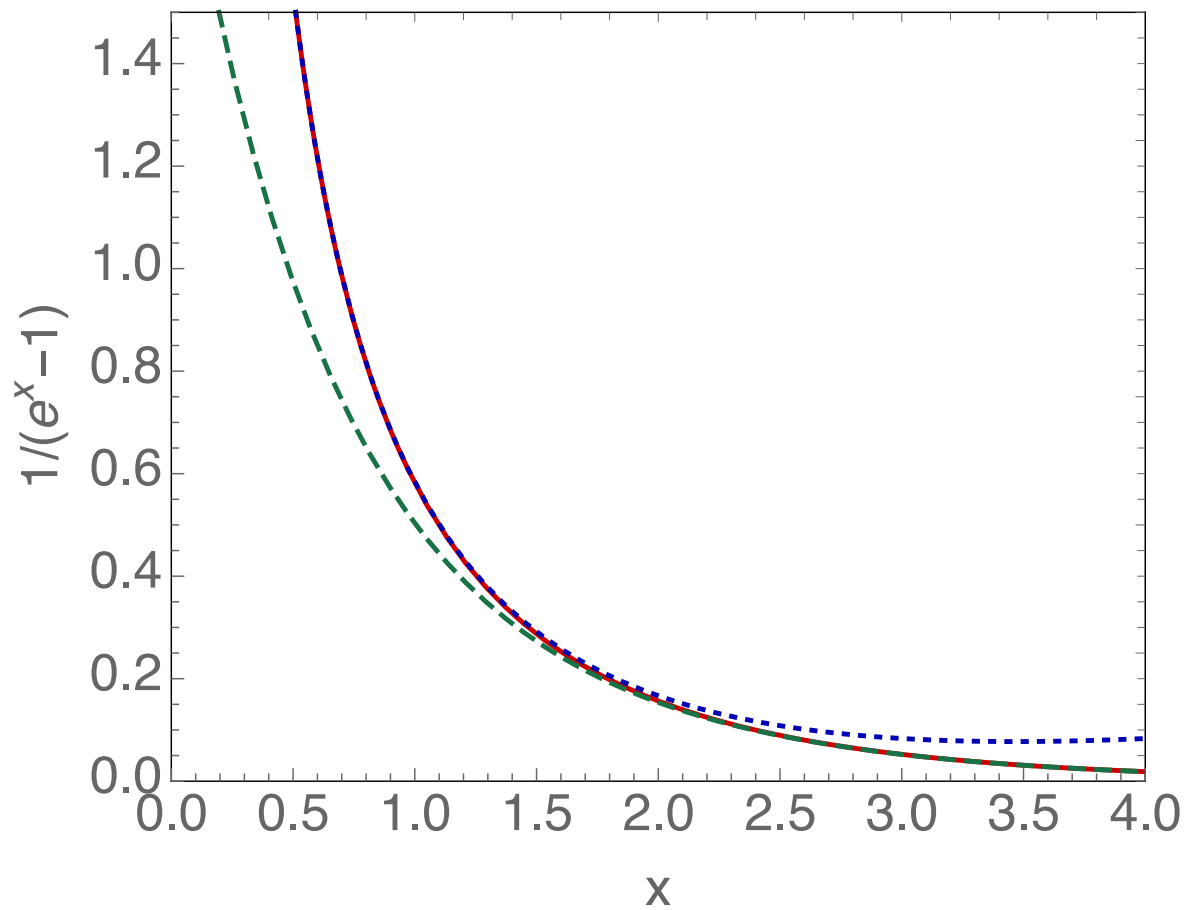$$\log(1 - e^{-x}) \simeq \log x - \frac{x}{2} + \frac{x^2}{24} + O(x^3)$$

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.

Problem 3.   Energy of the quantum harmonic oscillator

Recall from previous homework that the mean energy of a single classical harmonic oscillator interacting with the thermal environment is

$$\langle \epsilon \rangle = kT \tag{22}$$

Now we will compare this classical result to the quantum version of the harmonic oscillator. This builds on the previous which worked out the partition function.

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

(a) Determine the average energy $\langle \epsilon \rangle$ of the quantum harmonic oscillator at temperature T or $\beta = 1/kT$, using the partition function from a previous homework. Express your result using β and $\hbar\omega_0$. You can check your result using the next item.

(b) How is the mean vibrational quantum number $\langle n \rangle$ related to $\langle \epsilon \rangle$? Plot the mean number of vibrational quanta $\langle n \rangle$ versus $kT/\hbar\omega_0$ for $kT/\hbar\omega_0 = 0 \ldots 4$. Determine (from your graph) the temperature in units of $\hbar\omega_0$ where $\langle n \rangle = 1$. I find $T = 1.4427\,\hbar\omega_0/k_B$. Compare your exact number 1.4427 to your graphical estimate from the estimate previous homework.

(c) Plot
$$\frac{\langle \epsilon \rangle}{kT} \tag{23}$$
versus $kT/\hbar\omega_0$ for $kT/\hbar\omega_0 = 0 \ldots 4$.

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

$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\hbar\omega_0/kT} \tag{24}$$

or more generally
$$\langle \epsilon \rangle \simeq \hbar\omega_0 e^{-\beta\hbar\omega_0} \left(1 + e^{-\beta\hbar\omega_0} + \ldots \right) \tag{25}$$

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

$$\langle \epsilon \rangle \simeq kT \tag{26}$$

or more generally
$$\langle \epsilon \rangle \simeq kT \left(1 - \frac{\hbar\omega_0}{2kT} + \ldots \right) \tag{27}$$

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

(e) Consider a *classical* harmonic oscillator. Determine the mean energy $\langle \epsilon \rangle$ in the classical case, using any method you like from previous homework. Now reexamine the *quantum* result and notice that in the high temperature limit $T \gg \hbar\omega_0$ is

$$\lim_{T \to \infty} \langle \epsilon \rangle \simeq kT \tag{28}$$

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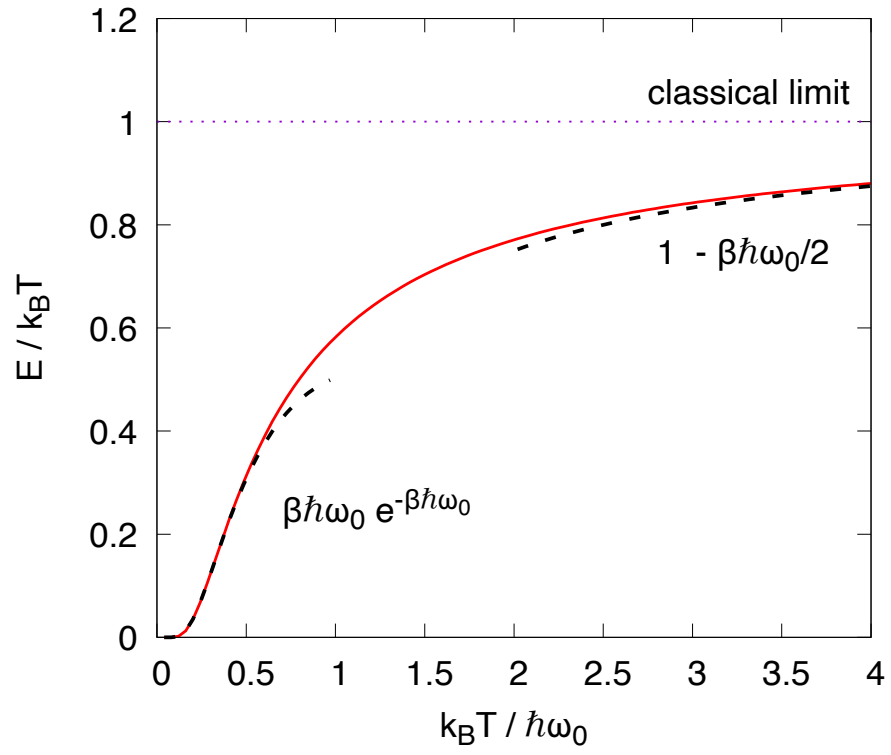
Figure 2: The energy $\langle \epsilon \rangle / kT$. Together with the expansions developed at large and small temperatures

(i) What is the percent change in energy for a quantum harmonic oscillator which transitions from the energy level with $n = 1$ to the energy level with $n = 2$? What about from $n = 1000000$ to $n = 1000001$?

(ii) Explain why at high temperatures the $\langle \epsilon \rangle$ of the quantum oscillator agrees with the classical one by discussing the significance of the graph in part (b) and of (e.i).

Hint: When as a function of temperature is discrete nature of the energy levels truly important?

(f) Consider a diatomic ideal gas. Recall that the mean energy of each molecule consists of a classical contribution from translational degrees of freedom $\frac{3}{2}kT$, plus a classical contribution from the rotational degrees of freedom $\frac{2}{2}kT$. Now, a quantum mechanical contribution from the vibrations can added. The energy computed in part (a) is the contribution of the vibrational motion, and was computed quantum mechanically. As discussed in class, the total energy for an ideal gas takes the form

$$U = Ne_0(T) \tag{29}$$

and is independent of the volume.

(i) What is $e_0(T)$? (Hint: just read the question!)

(ii) What are C_V and C_p? You should find that the specific heat C_p is

$$C_p = Nk_B \left[\frac{7}{2} + \frac{(\beta \hbar \omega_0)^2 e^{-\beta \hbar \omega_0}}{(1 - e^{-\beta \hbar \omega_0})^2} \right] \tag{30}$$

and that the specific heat per mole

$$C_p^{1\text{ml}} = R \left[\frac{7}{2} + \frac{(\beta \hbar \omega_0)^2 e^{-\beta \hbar \omega_0}}{(1 - e^{-\beta \hbar \omega_0})^2} \right] \tag{31}$$

(iii) Recall that for diatomic hydrogen the first vibrational frequency is $\hbar \omega_0 \simeq 0.54 \, \text{eV}$. Using this number together with $k_B = 0.025 \, \text{eV}/300 \, ^\circ \text{K}$, I made a graph of Eq. (31) that is shown below. Compare the result to the experimental data. What qualitatively does the (simple-minded) calculation get right and wrong? Explain.

Energy of SHO

a) We have

$$Z = \frac{1}{1 - e^{-\beta\hbar\omega_0}}$$

Then

$$\langle E \rangle = -\frac{\partial}{\partial\beta}\log Z = +\frac{\partial}{\partial\beta}\log(1 - e^{-\beta\hbar\omega_0})$$
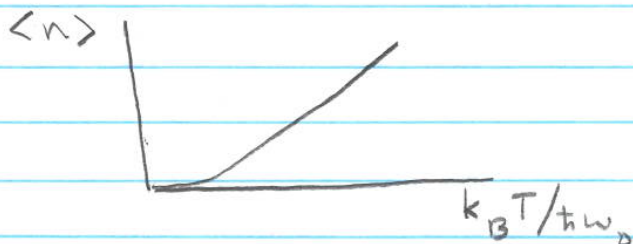
$$= \frac{1}{1 - e^{-\beta\hbar\omega_0}} e^{-\beta\hbar\omega_0}\,\hbar\omega_0$$

$$\boxed{\langle E \rangle = \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1}}$$

b) Then

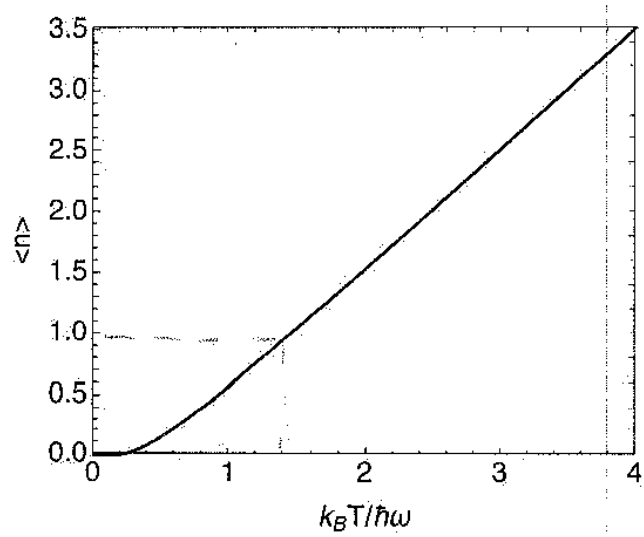$$\frac{\langle E \rangle}{\hbar\omega_0} = \frac{1}{e^{\hbar\omega/kT} - 1} = \langle n \rangle$$

Then

Then from graph

$$\langle n \rangle = 1 \quad \text{when}$$

$$k_B T / \hbar\omega_0 = 1.45$$

or

$$\boxed{k_B T = 1.45\, \hbar \omega_o}$$

(c) Then a nice plot of $\langle E \rangle$ is given in the problem statement.

(d) Using the series of problem 1

with $x \equiv \hbar \omega / kT$

at low temperature $kT \ll \hbar \omega_o$ then $x \gg 1$, and

$$\frac{1}{e^x - 1} = \frac{e^{-x}}{1 - e^{-x}} \simeq e^{-x}(1 + e^{-x} + \dots)$$

And

$$\boxed{\langle E \rangle = \hbar \omega_o\, e^{-\beta \hbar \omega_o}(1 + e^{-\beta \hbar \omega_o} + \dots)}$$

At high temperature $x \ll 1$

$$\frac{1}{e^x - 1} \simeq \frac{1}{x} - \frac{1}{2}$$

$$\langle E \rangle = \hbar \omega_o \left(\frac{k_B T}{\hbar \omega_o} - \frac{1}{2} \right) \simeq k_B T \left(1 - \frac{\hbar \omega_o}{2kT}\right)$$

(e) At high temperature the number of quanta $\langle n \rangle$ is very large. In this regime $\langle n \rangle \gg 1$, quantum mechanics becomes continuous, $\frac{\Delta E}{E} \ll 1$, and it approaches classical mechanics

This is the Bohr correspondence principle

f) We have

i)
$$U = N \left[\frac{8}{2} kT + \underbrace{\frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1}}_{\text{this is } f_0(T)} \right]$$

Then

ii)
$$C_v = \left(\frac{dU}{dT} \right)_V = N \left[\frac{5}{2} k + \frac{-\hbar \omega_0 e^{\beta \hbar \omega_0}}{(e^{\beta \hbar \omega_0} - 1)^2} \, \hbar \omega_0 \, \frac{\partial}{\partial T} \frac{1}{kT} \right]$$

$$= N \left[\frac{5k}{2} + \frac{(\beta \hbar \omega_0)^2 \, e^{\beta \hbar \omega_0} \, k}{(e^{\beta \hbar \omega_0} - 1)} \right]$$

$$C_v = Nk \left[\frac{5}{2} + \frac{(\beta \hbar \omega_0)^2 \, e^{\beta \hbar \omega_0}}{(e^{+\beta \hbar \omega_0} - 1)^2} \right]$$

So

$$C_p = C_v + Nk_B$$

$$C_p = Nk_B \left[\frac{7}{2} + \frac{(\beta \hbar \omega_o)^2}{(e^{\beta \hbar \omega_o} - 1)^2} \right]$$

iiv) So we see that the model nicely captures the transition from $C_p = \frac{7}{2} = 3.5$ to $\frac{9}{2} = 4.5$

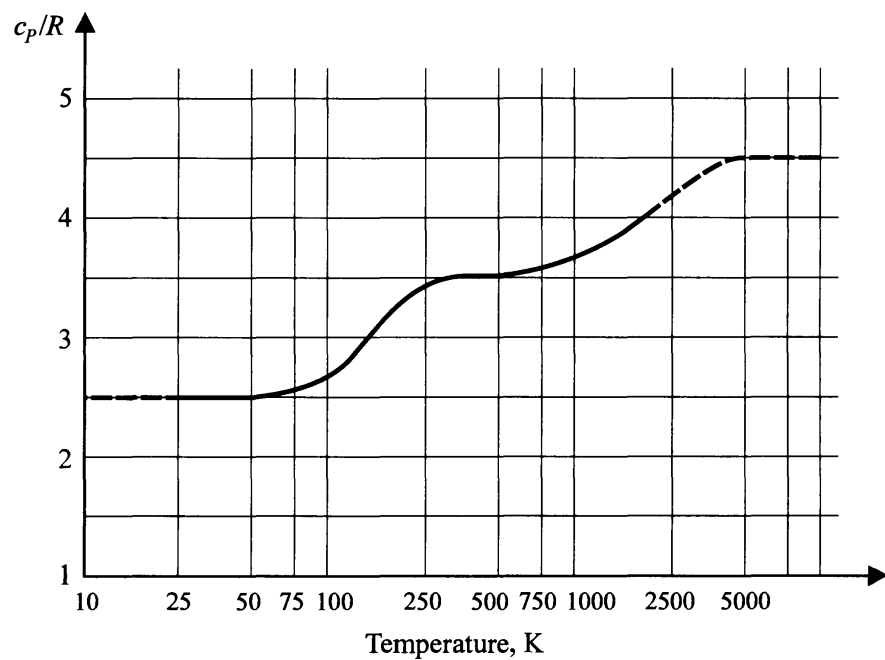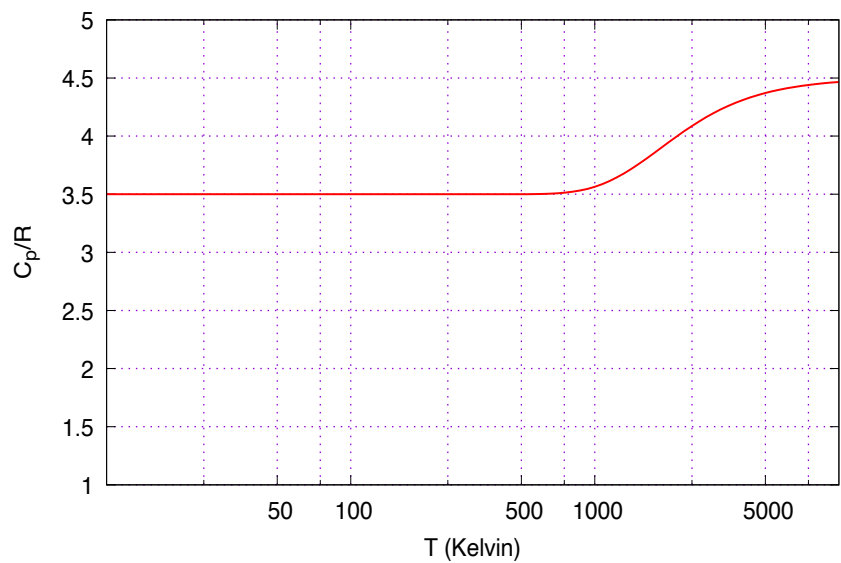but misses the transition to $\frac{5}{2}$ at low temperatures

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

Problem 4. Phase Space and Entropy of a MAIG

The phase space volume is a measure of the total number of possible ways for N of particles to *share* (or partition) the total energy and volume. For instance one particle could have almost all the available energy and the remaining $N-1$ particles could have very little. Such configurations are unlikely since they occupy only a small portion of the available phase space volume.

Consider a single particle in three dimensions in a box

$$0 < x, y, z < L \tag{32}$$

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

$$E < \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} < E + \delta E \,, \tag{33}$$

The particle is free to move around in phase space but the energy must lie in this range. $\delta E/E$ is the precision in the energy and should be considered small, say 10^{-4}. Your should realize that this means that the momentum is confined to a spherical shell between $p \equiv \sqrt{2mE}$ and $p_{\max} = \sqrt{2m(E + \delta E)}$.

(a) Show that the accessible phase space volume is

$$V_{\text{ps}} = \int_{[E,E+\delta E]} d^3\boldsymbol{r} d^3\boldsymbol{p} = V \left[4\pi \, (2mE)^{3/2} \frac{\delta E}{2E} \right] \tag{34}$$

Hint: Show that the thickness of the shell in momentum space is

$$\delta p \equiv p_{\max} - p \simeq p \frac{\delta E}{2E} \tag{35}$$

To count the number of configurations, divide up the phase space volume into cells of (arbitrary) small size $h = \Delta x \Delta p_x$, or in three dimensions cells of size[2]

$$h^3 = (\Delta x \Delta y \Delta z)(\Delta p_x \Delta p_y \Delta p_z) \tag{36}$$

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

$$\Omega(E, V) = \frac{1}{h^3} \int_{[E,E+\delta E]} d^3\boldsymbol{r} d^3\boldsymbol{p} \tag{37}$$

$$= V \left(\frac{2mE}{h^2} \right)^{3/2} 4\pi \frac{\delta E}{2E} \tag{38}$$

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[2]Classically this cell size was arbitrary. With the advent of quantum mechanics, it was realized that a natural choice for the cell size is Plank's constant h. But here let's understand it from a classical perspective first, choosing the cell size to be h somewhat arbitrarily.

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

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

$$\Omega(E, V) = \frac{1}{2!} \int_{[E, E+\delta E]} \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 p_1}{h^3} \frac{\mathrm{d}^3 r_2 \mathrm{d}^3 p_2}{h^3}. \tag{39}$$

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) Show that for two particles in three dimensions the number of accessible configurations is

$$\Omega(E, V) = V^2 \left(\frac{2mE}{h^2} \right)^3 \pi^3 \frac{\delta E}{4E}. \tag{40}$$

Hint: It is helpful to recall that the area of a sphere in d dimensions is given by a general formula

$$A_d = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1}. \tag{41}$$

In class we showed that for N particles with total energy E and volume V, the total the number of configurations and corresponding entropy of the system are given by

$$\Omega(E, V) = C(N) V^N E^{3N/2} \tag{42}$$

$$S(E, V) = k_B \ln \Omega = \frac{3}{2} N k_B \log E + N k_B \log V + \text{const}. \tag{43}$$

In the remainder of the exercise we will keep track of the constant $C(N)$.

(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 between E and $E + \delta E$) is

$$\Omega(E, V) = \frac{1}{N!} \int \frac{\mathrm{d}^3 r_1 \mathrm{d}^3 p_1}{h^3} \cdots \frac{\mathrm{d}^3 r_N \mathrm{d}^3 p_N}{h^3}, \tag{44}$$

$$= \frac{1}{N!} V^N \left(\frac{2\pi m E}{h^2} \right)^{3N/2} \frac{1}{\Gamma(3N/2)} \frac{\delta E}{E}. \tag{45}$$

N is large and is of order Avogadro's number.

(d) Use the Stirling approximation to show that[3]

$$\Omega(E, V) \simeq e^{5N/2} \left(\frac{V}{N} \right)^N \left(\frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3N/2}, \tag{47}$$

$$\tag{48}$$

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[3]For large n

$$\Gamma(n) \equiv (n-1)! \simeq n! \simeq (n/e)^n \tag{46}$$

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

and that the entropy is

$$S(E,V) = N k_B \log\left[\left(\frac{V}{N}\right)\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2}N k_B, \tag{49}$$

$$= N k_B \left[\log\left(\frac{v_N}{\lambda_{\text{th}}^3}\right) + \frac{5}{2}\right]. \tag{50}$$

Here $v_N = V/N$ is the volume per particle and

$$\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{4\pi m E/(3N)}}, \tag{51}$$

is the typical de Broglie wavelength at temperature T. The temperature is determined by the energy per particle for a monoatomic gas, $E/N = \frac{3}{2}k_B T$.

Hint: The $\delta E/E$ term is not exponentially large in contrast to the other terms. Thus $\delta E/E$ can be set to one via the following approximation:

$$e^{5N/2}\left(\frac{\delta E}{E}\right) = e^{5N/2 + \log(\delta E/E)} \simeq e^{5N/2}. \tag{52}$$

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.

Discussion: The result for S in Eq. (50) is known as the Sackur Tetrode equation and is fundamental. The Sackur-Tetrode equation says that the entropy per particle $S/N k_B$ is of order the logarithm of the accessible phase space per particle in units of h^3. Roughly speaking each particle has volume $v_N = V/N$. The *typical* momentum of a particle is of order $p_{\text{typ}} \sim \sqrt{m k_B T}$. The phase space per particle is the coordinate space volume v_N times the momentum space volume $\sim p_{\text{typ}}^3$ and is of order

$$V_{\text{ps}} \sim v_N \, p_{\text{typ}}^3. \tag{53}$$

The entropy per particle (divided k_B) is the logarithm of this phase space in units of h^3 and is of order

$$\frac{S}{N k_B} \sim \log\left(\frac{v_N \, p_{\text{typ}}^3}{h^3}\right) \sim \log\left(\frac{v_N}{\lambda_{\text{th}}^3}\right). \tag{54}$$

This logarithm is never very large (at most 10), and in practice the entropy per particle is an order one number.

(e) Recall that "Normal Temperature and Pressure" (NTP) is a temperature of $T^\ominus \equiv 298\,°\text{K}$ and $p^\ominus \equiv 1\,\text{bar}$. Show that the entropy per particle is

$$\frac{S}{N k_B} \simeq 13.1 - \ln(p/p^\ominus) + \frac{5}{2}\ln(T/T^\ominus) + \frac{3}{2}\ln(m/m_H) \tag{55}$$

Here m_H is the mass of a hydrogen atom and $13.1 = 10.6 + 5/2$. *Hint:* What is the entropy of Hydrogen gas at NTP?

(i) Use the result to evaluate the entropy per particle $S/N k_B$ of Argon at $200\,°\text{C}$ and two bars of pressure? (Ans: 19.3)
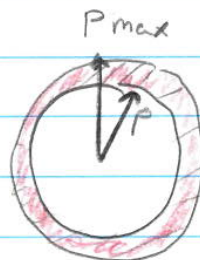
Phase Space

a) $\quad V_{PS} = \int d^3r \, d^3p \underset{[E, E+\delta E]}{} = V \int d^3p$

shell with energy
in range $[E, E+\delta E]$

$\quad = V \; 4\pi p^2 \, \delta p$

P_{max}

Then

$\quad P = \sqrt{2mE}$

See lecture!

$\quad P_{max} = \sqrt{2m(E+\delta E)}$

$\delta p = P_{max} - p = \sqrt{2mE} \left(1 + \delta E / E\right)^{1/2} - \sqrt{2mE}$

$\quad \simeq \sqrt{2mE} \left(1 + \frac{1}{2} \frac{\delta E}{E}\right) - \sqrt{2mE}$

$\quad \delta p = p \frac{\delta E}{2E} \qquad i.e. \qquad \frac{\delta p}{p} = \frac{\delta E}{2E}$

So

$$V_{PS} = V \; 4\pi p^3 \frac{\delta E}{2E} = V \left[4\pi (2mE)^{3/2} \frac{\delta E}{2E} \right]$$

b) Then

$$\Omega(E,V) = \frac{1}{2!} \int \frac{d^3r_1\, d^3p_1}{h^3} \cdot \frac{d^3r_2\, d^3p_2}{h^3}$$

$$= \frac{V^2}{2!} \underbrace{\int_{[E,\,E+\delta E]} \frac{d^3p_1\, d^3p_2}{h^6}}_{\text{shell volume}/h^6}$$

The momentum integral is a spherical shell in 6 dimensions
The momentum space volume is:

$$\frac{\text{Shell volume}}{h^6} = \frac{2\pi^{6/2}}{\Gamma(6/2)} p^5 \frac{\delta p}{h^6}$$

As before

$$\delta p = p \frac{\delta E}{2E}$$

So

$$p = \sqrt{2mE}$$

$$\Omega(E,V) = \frac{V^2}{2!} \frac{2\pi^3}{2!} \left(\frac{p}{h}\right)^6 \frac{\delta E}{2E}$$

$$\boxed{\Omega(E,V) = V^2 \pi^3 \left(\frac{2mE}{h^2}\right)^3 \cdot \frac{\delta E}{4E}}$$

c) Now the general case

$$\Omega(E,V) = \frac{1}{N!} \int \frac{d^3r_1 \, d^3p_1}{h^3} \cdots \frac{d^3r_N \, d^3p_N}{h^3}$$

$$= \left(\frac{V^N}{N!}\right) \int_{[E, E+\delta E]} (d^3p_1 \cdots d^3p_N) / h^{3N}$$

↗ coordinate space

momentum space

shell volume / h^{3N}

So this is again a shell of dimension $3N$

$$\frac{\text{Shell volume}}{h^{3N}} = \not{2} \frac{\pi^{3N/2}}{\Gamma(3N/2)} \left(\frac{p}{h}\right)^{3N} \frac{\delta E}{\not{2} E}$$

Using $\frac{p}{h} = \left(\frac{2mE}{h^2}\right)^{1/2}$ we get:

momentum space

$$\Omega(E,V) = \left(\frac{V^N}{N!}\right)\left(\frac{1}{\Gamma(3N/2)} \left(\frac{2\pi m E}{h^2}\right)^{3N/2}\right) \frac{\delta E}{E}$$

↗ coordinate space

d) Writing

$$N! = \left(\frac{N}{e}\right)^N \, , \quad \Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2e}\right)^{3N/2}$$

We have

$$\Omega(E,V) = \left[e^N \left(\frac{V}{N} \right)^N \right] \cdot \left[e^{3N/2} \left(\frac{4\pi m E}{3 N h^2} \right)^{3N/2} \right] \frac{\delta E}{E}$$

Taking the log of this expression, and dropping the $\delta E/E$ term, we have

$$S = k \ln \Omega$$

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

The term: $\left(\frac{4\pi m E}{N h^2} \right)^{3/2} = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} = \left(\frac{1}{\lambda_{th}^2} \right)^{3/2} = \frac{1}{\lambda_{th}^3}$

Where we used $\frac{E}{N} = \frac{3}{2} kT$

So finally

$$S = Nk \left[\ln \left(\frac{V_N}{\lambda_{th}^3} \right) + \frac{5}{2} \right]$$

↖ we will derive this in other ways as the course progresses. Here we have derived it from the microcanonical ensemble. Later we will derive it from the canonical ensemble.