# Problem 1. Working with the speed distribution

Consider the Maxwell speed distribution

(a) In three dimensions, evaluate the most probable speed $v_*$, i.e the speed where $P(v)$ is maximized. You should find $v_* = (2kT/m)^{1/2}$.

(b) Repeat (a) in two dimensions. You should find $v_* = (kT/m)^{1/2}$.

(c) (Optional) Determine the probability to have speed in a specific range, $v_* < v < 2v_*$. Follow the following steps:

    (i) Write down the appropriate integral.

    (ii) Change variables to a dimensionless speed $u = v/\sqrt{k_B T/m}$, i.e. $u$ is the speed in units of $\sqrt{k_B T/m}$, and express the probability as an integral over $u$.

    (iii) Write a short program (in any language) to evaluate the dimensionless integral, by (for example) dividing up the interval into 200 bins, and evaluate the integral with Riemann sums. You should find

$$\mathscr{P} \simeq 0.53 \tag{1}$$

## Speed Distribution

So

a)     $P(v)\, dv = \left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv$

- Maximizing $P(v)$ we have

$$P(v) = C\, e^{-v^2/2\sigma^2} v^2 \quad \text{with} \quad \sigma \equiv \left(\dfrac{kT}{m}\right)^{1/2}$$

$$P' = C\, e^{v^2/2\sigma^2}\left(\dfrac{v^3}{\sigma^2} + 2v\right)$$

- So $P$ is maximized when $P'(v) = 0$ or

$$v^2 = 2\sigma^2 \implies \boxed{v_* = \sqrt{\dfrac{2kT}{m}}}$$

For the 2d results see below

b)     $\mathcal{P} = \displaystyle\int_{v_*}^{2v_*} \left(\dfrac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, 4\pi v^2\, dv$

- Substituting

$$u = \dfrac{v}{(kT/m)^{1/2}} \quad \text{this becomes}$$

$$\mathcal{P} = \int_{\sqrt{2}}^{2\sqrt{2}} \frac{1}{(2\pi)^{3/2}} 4\pi \, e^{-u^2/2} \, u^2 \, du$$

- So

$$\mathcal{P} = \sqrt{\frac{2}{\pi}} \int_{\sqrt{2}}^{2\sqrt{2}} e^{-u^2/2} u^2 \, du$$

$$\approx 0.53$$

See program

In two dimensions the speed distribution is

$$P(v) = \frac{m}{2\pi kT} e^{-\frac{1}{2}mv^2/kT} 2\pi v = Ce^{-v^2/2\sigma^2} v$$

where $\sigma = \sqrt{kT/m}$. Differentiating to find the maximum (where $P'(v) = 0$) we have

$$P'(v) = Ce^{-v^2/2\sigma^2}\left(-\frac{v^2}{\sigma^2} + 1\right) = 0$$

Leading to $v_* = \sigma = \sqrt{kT/m}$.

```python
from math import *

xmin = sqrt(2.)
xmax = sqrt(2.)*2.

n = 1000
dx = (xmax - xmin)/n

s = 0.
for i in range(0, n):
    x = i * dx + xmin
    s = s + dx * sqrt(2./pi) * exp(-x*x/2.) * x * x
    print(s)
```

## Problem 2.   Einstein Model of Solid

A solid consists of an array of atoms in a crystal structure shown below. In a simple model (used by Einstein at the advent of quantum mechanics) each atom is assumed to oscillate independently of every other atom[1]. The model has one free parameter $\omega_0$ and predicts the general properties of specific heats of solids.

In one dimension a "solid" of $N$ atoms consists of $N$ independent harmonic oscillators. The Hamiltonian of each oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \tag{2}$$

where $m$ is the mass of the atom. In two dimensions each atom can oscillate in the $x$ direction and the $y$ direction. Thus, the solid of $N$ atoms consists of $2N$ independent quantum oscillators. The Hamiltonian (or energy) of each atom is a sum of two harmonic oscillators:

$$H = H_x + H_y \tag{3}$$
$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) \tag{4}$$

Finally in three dimensions (shown below) the solid of $N$ atoms consists of $3N$ independent oscillators as shown below, and each atom can oscillate in the $x$, $y$, or $z$ directions. The Hamiltonian of each atom shown in Fig. 1 consists of three harmonic oscillators:

$$H = H_x + H_y + H_z \tag{5}$$
$$= \left(\frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2\right) + \left(\frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2\right) + \left(\frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2 z^2\right) \tag{6}$$

The total Hamiltonian is a sum of the Hamiltonians of each atom.

(a) By appealing to the equi-partition theorem for a classical harmonic oscillator, argue that the mean energy of the solid at temperature $T$ is

$$E = 3NkT, \tag{7}$$

   if the solid is treated as $3N$ independent classical oscillators. Determine the specific heat $C_V^{\text{1ml}}$ for one mole of substance in this case.

(b) When each the solid is treated as $3N$ quantum harmonic oscillators, the energy of the solid is $E = 3N\langle\epsilon\rangle$, where the $\langle\epsilon\rangle$ is the average energy of the a single harmonic oscillator. By reviewing the results of previous homework, write down the total energy of the solid at temperature $T$, and record the mean vibrational quantum number $\bar{n}$ of a single oscillator.

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[1]In reality the motions of the atoms are coupled to each other, and the oscillation pattern of the solid, may be found by breaking it up into normal modes.
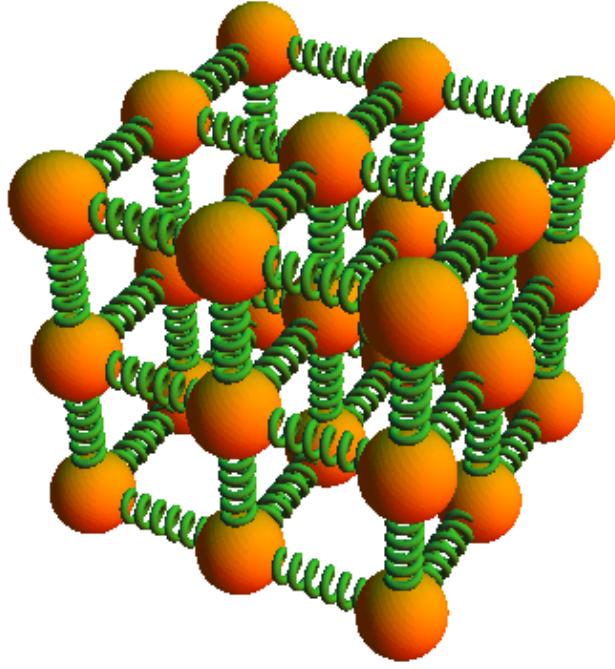
Figure 1:

(c) The figure below shows $N = 400$ harmonic oscillators in equilibrium sharing the total available energy. The numbers indicate the energy level $n$ of each oscillator – if one oscillator gains a unit of energy, e.g. increasing from $3\,\hbar\omega_0$ to $4\,\hbar\omega_0$, the rest of the oscillators will have one less unit of energy to share. Estimate the temperature of the system.

```
1 0 1 0 2 1 0 0 2 1 3 1 1 1 0 0 0 0 1 0
1 2 2 2 0 0 0 0 0 0 1 1 0 0 3 5 1 0 0 0
0 0 1 1 0 2 0 0 6 1 1 0 1 1 1 0 2 0 0 0
0 3 3 0 0 2 0 0 3 0 1 3 0 2 0 0 0 3 0 0
2 0 0 1 0 6 0 4 1 0 0 0 2 1 0 0 1 1 1 0
1 0 6 0 4 0 1 2 1 0 0 0 1 0 0 0 0 3 4 1
0 0 0 1 2 4 0 0 1 0 0 2 0 1 2 1 1 2 0 6
1 3 0 0 2 0 1 0 1 0 0 3 0 4 0 2 1 0 6 1
1 1 1 0 0 0 0 1 0 3 1 2 0 0 0 0 1 0 0 0
0 0 0 0 0 2 0 3 1 0 0 0 0 3 0 0 2 2 1
9 1 0 1 1 0 2 1 0 1 0 0 0 3 7 3 0 2 3 0
2 2 0 0 0 0 0 1 0 1 7 1 3 1 0 1 3 0 1 0
0 5 3 0 1 2 4 8 1 0 4 0 3 0 1 0 0 0 4 0
0 0 0 0 1 0 0 0 0 1 0 1 0 0 2 3 0 2 0 0
0 1 1 0 0 2 0 4 0 1 0 4 0 1 1 1 1 8 5 1
0 0 0 0 1 0 0 0 2 0 1 0 1 1 2 0 0 1 1 1
3 0 0 0 4 0 0 1 0 1 2 0 0 1 2 0 2 0 1 0
0 0 1 2 1 0 0 0 0 0 1 0 0 0 2 0 1 1 0 0
1 0 1 0 0 0 1 0 3 1 0 0 0 0 0 2 9 0 0 5
0 0 1 2 3 0 1 2 0 2 4 0 0 0 1 2 0 0 0 1
```

(d) Show that the specific heat $C_V$ for one mole of solid is[2]

$$C_V^{1\,\mathrm{ml}} = 3R\frac{(\beta\hbar\omega_0)^2 \exp(-\beta\hbar\omega_0)}{(1 - \exp(-\beta\hbar\omega_0))^2} . \tag{9}$$

Make a Taylor series expansion of $C_V^{1\,\mathrm{ml}}$ at high temperature, including the just leading term. What is the specific heat in the ultimate high temperature limit? Your result should be consistent with part (a). Why?

(e) Download a text file with the experimental data on the specific heat of silver[3], see here. Make a graph of the data, and the Einstein prediction for $C_V^{1\,\mathrm{ml}}$ for $\hbar\omega_0 = 4E_0, 2E_0, E_0, E_0/2, E_0/4$ with $E_0 = 0.013\,\mathrm{eV}$. $E_0$ was a free parameter in the Einstein model. The graph I get for silver is shown below as well as the $C_V$ for other substances:

(i) Diamond is known to be a very hard substance. Loosely explain how this fact is reflected in the data on $C_V$ presented in the figure below? *Hint*: What does the graph of $C_V$ for different substances tell you about the relative strengths of the spring constants of the material?

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[2]It is generally when computing $C_V$ to recognize that

$$T\frac{\partial}{\partial T} = -\beta\frac{\partial}{\partial \beta} \tag{8}$$

[3]The file contains two columns, the first is the temperature in Kelvin, the second is the specific heat in units of $J/(\mathrm{mol}\,K)$

# Einstein Solid

**a)** There are 3N oscillators. The Hamiltonian of the oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2$$

two quadratic forms

So, $\bar{E} = 3N \times 2 \times \frac{1}{2}kT \simeq 3NkT$

Now $C_v = \partial E / \partial T$.

So for $N = 1$ mol

$N_A k_B = R$, and so

$$C_v^{1ml} = 3R$$

**b)** $E = 3N \dfrac{\hbar\omega}{e^{\beta\hbar\omega}-1}$ $\qquad \bar{n} = \dfrac{1}{e^{\beta\hbar\omega}-1}$

**c)** Solving for $\beta$ from $\bar{n}$ (to make contact with later work in the next problem)

$$\frac{1}{\bar{n}} = e^{\beta\hbar\omega}-1 \implies e^{\beta\hbar\omega} = 1+\frac{1}{\bar{n}}$$

So

$$\beta\hbar\omega = \ln\left(\frac{1+\bar{n}}{\bar{n}}\right) \implies \frac{1}{kT} = \frac{1}{\hbar\omega}\ln\left(\frac{1+\bar{n}}{\bar{n}}\right)$$

Now we can estimate the $\bar{n}$ by counting up the numbers in the figure and dividing by 400 (the number of atoms). Doing this we find $\bar{n} = 1$. So $\beta\hbar\omega = \ln((1+1)/1) = \ln(2)$ and $kT = \hbar\omega/\ln(2)$.

**d)** We know that

$$C_V = \left(\frac{\partial E}{\partial T}\right) \quad \text{with} \quad E = 3N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

We use that for any quantity $X$

$$\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta} \frac{\partial \beta}{\partial T} = \frac{\partial X}{\partial \beta} \frac{\partial}{\partial T}\left(\frac{1}{kT}\right)$$

$$\boxed{\frac{\partial X}{\partial T} = -k\beta^2 \frac{\partial X}{\partial \beta}}$$

So

$$C_V = -k\beta^2 \frac{\partial}{\partial \beta}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right)$$

Differentiating

$$C_V = 3Nk\beta^2 \frac{(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

For 1 mol $N = N_A$ $N_A k_B = R$

$$\boxed{C_V^{1ml} = 3R \frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}}$$

In the high temperature limit the mean # of quanta in the oscillator gets larger and larger. In this limit the dynamics should be classical. (see previous homework)

Expanding for $\beta\hbar\omega \ll 1$ (high temperature), we approximate:

$$e^{\beta\hbar\omega} \simeq 1 + \beta\hbar\omega$$

And

$$C_v^{1ml} \simeq 3R (\beta\hbar\omega)^2 \frac{(1)}{(1 + \beta\hbar\omega - 1)^2}$$

$$\boxed{C_v^{1ml} \simeq 3R}$$

this agrees with part (a) as it should

(e)) The hard materials have a larger $\omega_o = \sqrt{k/m}$. They have, therefore, a larger spring constant, $k$. Because $\omega_o$ is higher for diamond $C_v$ will approach the classical limit $3R$ only at very high temperatures $kT \gg \hbar\omega_o$, when the number of vibrational quanta is large.
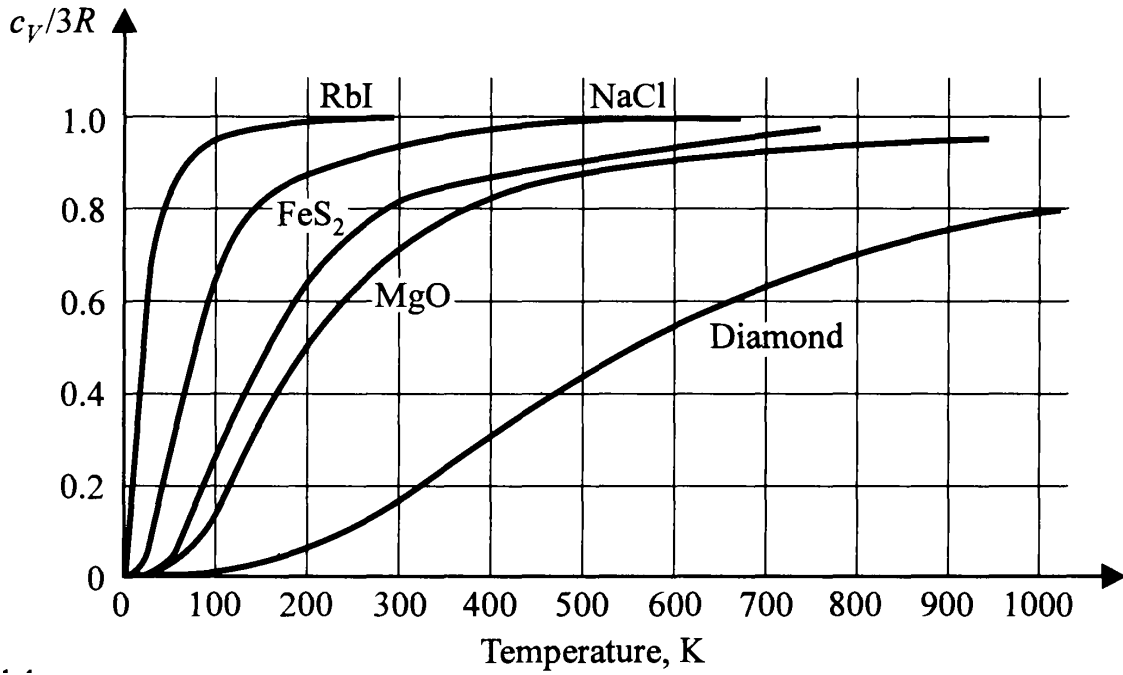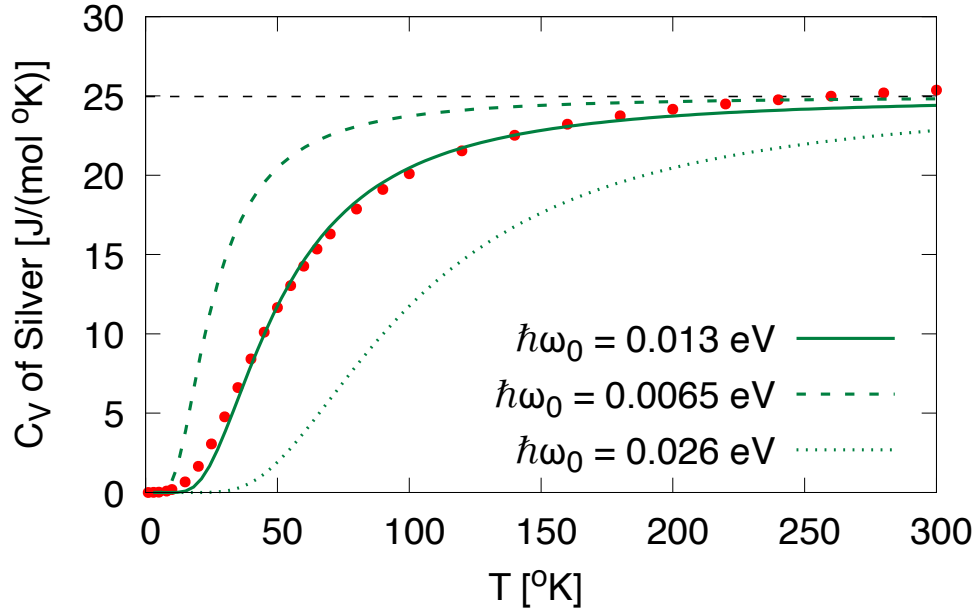
Figure 2: Specific heats of solids: (a) The Einstein Model with $\hbar\omega_0$ treated as a parameter compared to the specific heat of silver. The graph approaches $3R$ at high temperature. (b) The specific heat $C_V$ in units of $R$ of various solids versus temperature. The specific heat approaches $3R$ at high temperature

## Problem 3.    Entropy changes of a MAIG

Find the change in entropy of $n_{\mathrm{ml}}$ moles of an ideal monoatomic ideal gas in the following processes:

   (a) the temperature changes from $T_1$ to $T_2$ at constant pressure;

   (b) the pressure changes from $P_1$ to $P_2$ at constant volume.

Consider the expression for the number of states in a mono-atomic ideal gas

$$\Omega = C(N)V^N E^{3N/2} \,, \tag{10}$$

and the corresponding entropy

$$S = Nk_B \log(V) + \frac{3}{2}Nk_B \log(E) + \text{const} \,. \tag{11}$$

Recall that in an adiabatic expansion of a monoatomic ideal gas no heat enters or exits the system and the entropy remains constant as the volume increases.

   (c)  (i) Using Eq. (11) show that $\Delta S = 0$ for an adiabatic increase in volume from $V_1$ to $V_2$. (*Hint:* How does the temperature change during an adiabatic expansion of a mono-atomic ideal gas?)

     (ii) Describe how the particles are redistributed in phase space so that the entropy and total phase space volume remains constant during the expansion.

Ans: (a) $\frac{5}{2}n_{\mathrm{ml}}R\ln(T_2/T_1)$; (b) $\frac{3}{2}n_{\mathrm{ml}}R\ln(P_2/P_1)$.

## Entropy Changes of Ideal Gas

This is the entropy of a MAIG, which we derived. We will use this in this problem

($\star$) $\quad S = Nk \ln V + \dfrac{3Nk}{2} \ln E + const$

a) $\quad PV = NkT$, so for $P$ const, $\quad \dfrac{V_1}{V_2} = \dfrac{T_1}{T_2} = \dfrac{E_1}{E_2}$

Since $\quad E = \dfrac{3}{2} NkT \propto T$,

So

$\Delta S = S_2 - S_1$

$\quad = Nk \ln \dfrac{V_2}{V_1} + \dfrac{3Nk}{2} \ln \dfrac{E_2}{E_1}$

$\quad = Nk \ln \dfrac{T_2}{T_1} + \dfrac{3}{2} Nk \ln \dfrac{T_2}{T_1}$

$\boxed{\Delta S = \dfrac{5}{2} Nk \ln \dfrac{T_2}{T_1}}$

b) $\quad \Delta S = S_2 - S_1$

constant volum

$\quad = Nk \ln \dfrac{V_2}{V_1} + \dfrac{3}{2} Nk \ln \dfrac{E_2}{E_1} \quad now \quad PV = NkT$

$P \propto T \propto E$

So

$$\Delta S = \frac{3}{2} Nk \ln \left( \frac{P_2}{P_1} \right)$$

c) Now for an adiabatic expansion

$$T V^{\gamma - 1} = \text{const}$$

this is for a
MAIG

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma - 1}$$

where $\gamma = \frac{5}{3}$

or

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{2/3}$$

$$\frac{E_2}{E_1} = \frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{-2/3}$$

So

$$\Delta S = Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

(i)
$$= Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \left( \frac{V_2}{V_1} \right)^{-2/3} = 0$$

(ii) The coordinate space volume is getting bigger, but the momentum space volume is getting smaller as the temperature drops. We have
$$E V^{3/2} = \text{const} \quad \text{during the adiab expansion of a MAIG.}$$

## Problem 4.    Entropy change in the mixing of hot and cold gasses

| $N_1, T_1$ | $N_2, T_2$ |
|:---:|:---:|
| He | Ar |

Consider two mono-atomic ideal gasses, Helium and Argon, separated by a divider which partitions a container of volume $V$ into two equal parts. There are $N_1$ Helium atoms on the left of the divider, and $N_2$ Argon atoms on the right of the divider. The Helium atoms are initially at a temperature of $T_1$, while the Argon atoms are initially at a temperature of $T_2$. After the dividing wall is removed, the two gasses mix and ultimately equilibrate.

(a) Determine the final temperature of the system.

(b) Determine the change in entropy of the system resulting from the mixing process in two ways:

   (i) Directly count the number of states at the beginning and end.

   (ii) Calculate the change in entropy by identifying an equilibrium path connecting the state at the beginning and the state at the end and using thermodynamics. Explain how the example illustrates the formula the formula

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} > \frac{Q}{T} \tag{12}$$

# Entropy change in the mixing of Hot & Cold Gasses

(a) Energy is conserved and the gasses ultimately have the same temperature.

$$E_1 + E_2 = E$$

$$\frac{3}{2} N_1 k T_1 + \frac{3}{2} N_2 k T_2 = \frac{3}{2}(N_1 + N_2) k T$$

$$N_1 T_1 + N_2 T_2 = T$$
$$\overline{(N_1 + N_2)}$$

b) The entropy of Each Gas is

$$S = Nk \ln V + \frac{3}{2} Nk \ln E + cast$$

$$\left.\begin{array}{c} \\ \\ \end{array}\right\} E \propto T$$

$$S = Nk \ln V + \frac{3}{2} Nk \ln T + const$$

↖ a different constant

So

$$\Delta S = Nk \ln \frac{V_f}{V_i} + \frac{3}{2} Nk \ln T_f / T_i$$

Here we have two gasses:

$$\frac{V_f}{V_i} = \frac{V}{V/2} = 2 \qquad \frac{T_f}{T_i} = \frac{T}{T_1} \quad \text{for gas \#1}$$

$$\frac{T_f}{T_i} = \frac{T}{T_2} \quad \text{for gas \#2}$$

So

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$\Delta S = (N_1 + N_2) k \ln 2 \quad + \quad \frac{3}{2} N_1 k \ln \frac{T}{T_1} + \frac{3}{2} N_2 k \ln \frac{T}{T_2}$$

The thermodynamic argument for the change in entropy (just found) goes as follows. Take gas 1. It's initial state and final states are

$$(T_1, V_1 = \frac{V}{2}) \to (T_f, V) \tag{13}$$

Since entropy only depends on the state, and not on how you got there, we can pick any convenient equilibrium path to get from the initial state to the final state. The actual system did not follow this path. Then we can evaluate the entropy change using

$$dS = \frac{dQ_{\text{rev}}}{T} . \tag{14}$$

This formula assumes the system is in equilibrium with a reservoir at temperature $T$, which was not the case here. Here no heat flowed from the environment to the system. The initial and final states of gas 2 are

$$(T_2, V_2 = \frac{V}{2}) \to (T_f, V) \tag{15}$$

A convenient choice of path is: (*Step 1*) first leave the volume constant and increase the temperature; (*Step 2*) then leave the temperature fixed and increase the volume.

*Step 1*: In the first step the work done is zero since volume is constant. So $dQ_{\text{rev}} = C_V \, dT$ where $C_V = (3/2)N_1 k$ is the specific heat of a MAIG. Thus for gas number 1 in step 1 we have:

$$\Delta S_{1,1} = \int C_V \frac{dT}{T} = C_V \ln(T_f/T_i) = \frac{3}{2} N_1 k \ln(T_f/T_1) \tag{16}$$

Similarly for gas number 2 in step 1 one we have:

$$\Delta S_{2,1} = \frac{3}{2} N_2 k \ln(T_f/T_2) \tag{17}$$

*Step 2*: Then in the second step the temperature is constant, but the volume increases. The energy is also constant, since for an ideal gas the energy is only a function of temperature, which is constant. So, in the second step $dU = 0$ and $dQ_{\text{rev}} = p_1 \, dV$ by the first law ($dU = dQ - pdV$). Thus we find

$$\Delta S_{1,2} = \int \frac{dQ_{\text{rev}}}{T} = \int_{V_1}^{V} \frac{p_1}{T} dV = N_1 k \ln(2) \tag{18}$$

Similarly, for gas number 2 in step 2

$$\Delta S_{2,2} = N_2 k \ln(2) \tag{19}$$

Putting together the contributions, we find:

$$\Delta S = \Delta S_{1,1} + \Delta S_{2,1} + \Delta S_{1,2} + \Delta S_{2,2} \tag{20}$$

$$= (N_1 + N_2)k \ln(2) + \frac{3}{2} N_1 k \ln(T_f/T_1) + \frac{3}{2} N_2 k \ln(T_f/T_2) \tag{21}$$

which agrees with the previous method.

**Discussion:** In each step, we assumed that gas 1 and gas 2 were in equilibrated contact with a reservoir at temperature $T$. This approach is valid (although not reality) because we are using these fictitious reservoir to find the change in entropy of the system, which only depends on the initial and final states, which are in complete equilibrium. But, it must be understood that in reality no heat is exchanged with the environment and $dQ = 0$. In general the change in entropy of the system (which can be computed by assuming a reversible exchange of heat with a reservoir) is larger than the actual heat that flows into the system from a reservoir at temperature $T$:

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} > \frac{Q}{T} \tag{22}$$

In this specific problem $Q = 0$ and we found

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} = (N_1 + N_2)k\ln(2) + \frac{3}{2}N_1 k \ln(T_f/T_1) + \frac{3}{2}N_2 k \ln(T_f/T_2) > 0 \tag{23}$$

Clearly $\Delta S > 0$ and the process is irreversible.

# Problem 5.   Isothermal Atmosphere

Consider a gas at temperature $T$ near the earth's surface. The potential energy due to gravity is

$$U = mgz \tag{24}$$

where $z$ is height above the earth's surface, $z = 0$. Our goal is to use partition functions to evaluate the probability that a particle will have height $z$ above the earth's surface

For simplicity assume that the $x, y$ coordinates are in a large "box" of area $L^2$, but the height $z$ runs from zero (the earth's surface) to infinity (outer space), i.e.

$$0 < x, y < L \qquad 0 < z < \infty \tag{25}$$

The spatial coordinates are $\boldsymbol{r} = (x, y, z)$ and the momentum coordinates are $\boldsymbol{p} = (p_x, p_y, p_z)$

(a) Write down the Hamiltonian of a particle and compute the (single particle) partition function of the classical particle. You should find

$$Z_1 = \frac{L^2 \ell (2\pi m k T)^{3/2}}{h^3} \tag{26}$$

where $\ell \equiv kT/mg$. Express $Z_1$ using the thermal de Broglie wavelength. What are the units of $Z_1$ ?

(b) Determine the probability distribution

$$\mathrm{d}\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = P(\boldsymbol{r}, \boldsymbol{p}) \mathrm{d}^3\boldsymbol{r} \mathrm{d}^3\boldsymbol{p} \tag{27}$$

and show that it factorizes into probability of position $P(\boldsymbol{r})$ times a probability of momentum $P(\boldsymbol{p})$.

(c) By differentiating the partition function (or better $\ln Z$) find: (i) the mean energy $\langle \epsilon \rangle$, and (ii) the variance in the energy $\langle (\delta\epsilon)^2 \rangle$.

(d) Compute the mean height $\langle z \rangle$ in two ways:

    (i) Compute the probability distribution for height $z$, $\mathrm{d}\mathscr{P}_z$ by integrating over (or "marginalizing over") the unobserved coordinates. Sketch this distribution and use it to find the mean height $\langle z \rangle$.

    (ii) Use the equipartition to find the mean kinetic energy and combine this with your result $\langle \epsilon \rangle$ to determine the mean potential energy, $\langle U \rangle$. Are your results from (i) and (ii) consistent with each other?

(e) Make a reasonable estimate for this height in kilometers, by estimating the the typical mass of an air molecule, and a typical temperature.

Please do not substitute, $k_B = 1.38 \times 10^{-23} \mathrm{J}/{}^\circ\mathrm{K}^{-1}$, and try not to look up numbers. Rather puts the numbers in physical terms, and remember them. A list of useful constants that you need for this course is maintained on the web site.

(f) If the gas density at $z = 0$ is $n_0$, what is the density $n(z)$ at height $z$?

(g) A mechanical analysis of the forces in the the gas says that

$$\frac{dp(z)}{dz} = -mgn(z) \tag{28}$$

where $p(z)$ is the pressure in the gas at height $z$. Explain briefly the physical meaning of Eq. (28), and then show that part $(e)$ is consistent with Eq. (28) and the ideal gas law, $pV = n_{\mathrm{ml}}RT$ provided the temperature is constant.

**Solution**

(a) The Hamiltonian is the kinetic plus potential energy as a function of $\boldsymbol{p}$ and $\boldsymbol{r}$

$$\mathcal{H}(\boldsymbol{r},\boldsymbol{p}) = \frac{p^2}{2m} + mgz \tag{29}$$

with $p^2 = p_x^2 + p_y^2 + p_z^2$ the squared magnitude of the momentum. The partition function

$$Z_1 = \int \frac{d^3\boldsymbol{r}d^3\boldsymbol{p}}{h^3} e^{-p^2/2mkT} e^{-mgz/kT} . \tag{30}$$

The integration over the $x, y$ spatial coordinates gives $L^2$. The momentum integrations is the same as for the velocity distributions discussed in class

$$\int dp_x dp_y dp_z \, e^{-(p_x+p_y^2+p_z^2)/2mkT} = \left[ \int dp_x e^{-p_x^2/2mkT} \right]^3 = (2\pi mkT)^{3/2} . \tag{31}$$

The integral over $z$ is the new bit:

$$\int_0^\infty dz \, e^{-mgz/kT} = \frac{kT}{mg} \equiv \ell \tag{32}$$

In total we have

$$Z_1 = \frac{1}{h^3} L^2 \left( \frac{kT}{mg} \right) (2\pi mkT)^{3/2} \tag{33}$$

(b) We have

$$d\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \frac{1}{Z_1} e^{-\mathcal{H}(\boldsymbol{r},\boldsymbol{p})/kT} \frac{d^3\boldsymbol{r} \, d^3\boldsymbol{p}}{h^3} . \tag{34}$$

So the normalization constant is $Z_1 h^3$, leading to

$$d\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \left( \frac{e^{-p^2/2mkT}d^3p}{(2\pi mkT)^{3/2}} \right) \left( \frac{mg}{kT} e^{-mgz/kT}dz \right) \left( \frac{dx \, dy}{L^2} \right) . \tag{35}$$

In writing this expression we have put the factors that make up $Z$ underneath the differentials that they stemmed from, e.g.

$$\int dz e^{-mgz/kT} = \ell \qquad d\mathscr{P} \propto \frac{1}{\ell} e^{-mgz/kT} dz . \tag{36}$$

We see that the probability factorizes – it is a probability of momentum $\boldsymbol{p}$; times a probability of height $z$; times a probability of transverse coordinates $x, y$ (which is just a constant $1/L^2$).

(c) We need to compute

$$\langle \epsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{37}$$

$$\langle \delta\epsilon^2 \rangle = \frac{\partial \ln^2 Z}{\partial \beta^2} = -\frac{\partial \langle \epsilon \rangle}{\partial \beta} \tag{38}$$

We only need the dependence on $\ln Z$ on $\beta$. We see that $Z \propto \beta^{-5/2}$:

$$\ln Z = \ln(\beta^{-5/2}) + \text{const} \tag{39}$$

We do not need to be explicit about the constant as we are planning to differentiate the result. This simplification is extremely common. So,

$$\langle \epsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{5}{2}\frac{1}{\beta} = \frac{5}{2}kT \tag{40}$$

$$\langle \delta\epsilon^2 \rangle = \frac{\partial \ln^2 Z}{\partial \beta^2} = -\frac{\partial \langle \epsilon \rangle}{\partial \beta} = \frac{5}{2}\frac{1}{\beta^2} = \frac{5}{2}(kT)^2 \tag{41}$$

(d) We have

$$d\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \left(\frac{e^{-p^2/2m}d^3p}{(2\pi mkT)^{3/2}}\right)\left(\frac{mg}{kT}e^{-mgz/kT}dz\right)\left(\frac{dxdy}{L^2}\right) \tag{42}$$

$$= P(p_x, p_y, p_z)d^3p \times P(z)dz \times P(x,y)dxdy \tag{43}$$

By construction (look carefully at part (a)) each of the terms is separately normalized and the probability factorizes. Integrating over $p_x, p_y, p_z$, and over $x, y$ gives unity for each integral yielding

$$d\mathscr{P}_z = \int_{\text{over } x, y, p_x, p_y, p_z} d\mathscr{P}_{\boldsymbol{r},\boldsymbol{p}} = \frac{mg}{kT}e^{-mgz/kT} = \frac{1}{\ell}e^{-\ell}dz \tag{44}$$

with $\ell = kT/mg$. Then we can calculate

$$\langle z \rangle = \int_0^\infty P(z)dz = \int_0^\infty \frac{1}{\ell}e^{-z/\ell}dz \times z \tag{45}$$

Changing variables to $u \equiv z/\ell$ we find

$$\langle z \rangle = \ell \int_0^\infty e^{-u}du\,u \equiv \ell\,\Gamma(2) = \ell \tag{46}$$

An alternative way to proceed us to use that the mean kinetic energy is

$$\langle K \rangle = \left\langle \frac{p_x^2 + p_y^2 + p_z^2}{2m} \right\rangle = 3 \times \tfrac{1}{2}kT \tag{47}$$

i.e. the average of every quadratic form in the classical Hamiltonian (or energy as a function of as a function of position and momentum) is $\frac{1}{2}kT$. There are three quadratic forms in the kinetic energy. Then since the average energy is the sum of the average kinetic and average potential energy

$$\langle \epsilon \rangle = \langle K + mgz \rangle = \frac{5}{2}kT \tag{48}$$

we find

$$\langle mgz \rangle = kT \tag{49}$$

Thus as found above:

$$\langle z \rangle = \frac{kT}{mg}. \tag{50}$$

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(e) First we interpret the height $\ell$. The typical energy $\sim kT$. A particle with this kinetic energy on the earth's surface will fly to a height

$$\ell = \frac{kT}{mg} \, . \tag{51}$$

So, $\ell$ sets the scale for the height.

Now lets evaluate this for diatomic nitrogen (Air is 70% $N_2$). The molar mass of $N_2$ is $28\,\text{grams} = 0.028\,\text{kg}$ . Taking $R = 8.32\text{J}/°\text{K}$ and $T = 300\,°\text{K}$ we find

$$\ell = \frac{N_A kT}{N_A mg} = \frac{RT}{(0.028\,\text{kg})(9.8m/s^2)} \simeq 9.1\,\text{km} \tag{52}$$

(f) Clearly

$$\frac{n(z)}{n(0)} = \frac{P(z)}{P(0)} \tag{53}$$

So

$$n(z) = n(0)e^{-mgz/kT} \tag{54}$$

where $n(z)$ is the number of molecules per volume

(g) Take a slab of air of area $\mathcal{A}$ and draw a free body diagram (see figure). Since the forces must balance we must have

$$-\mathcal{A}\,p(z + dz) + \mathcal{A}\,p(z) - mg\,(\mathcal{A}dz)\,n(z) = 0 \, . \tag{55}$$

Here the first term is the pressure force pushing down on the slab; the second term is the pressure force pushing up on the slab; the third term is the weight of the slab (its volume is $dV = \mathcal{A}\,dz$ and there are $n(z)$ particles of mass $m$ per volume).

area $\mathcal{A}$

$\mathcal{A}\,p(z + dz)$

$dz$

Weight:

$\mathcal{A}\,p(z)$

$Mg = n(z)\,dV\,mg$
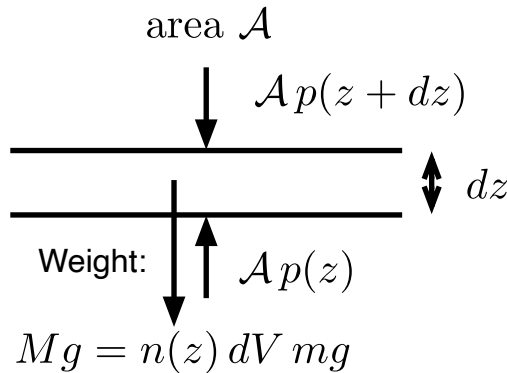
Thus

$$\frac{dp}{dz} = -mgn(z) \tag{56}$$

This equation used no statistical mechanics – it is only mechanics.

Now we use statistical mechanics to verify overall consistency. The pressure is given by the ideal gas law:

$$p(z) = \frac{NkT}{V} = n(z)kT = n(0)e^{-mgz/kT}\, kT\,. \tag{57}$$

Differentiating we have

$$\frac{dp}{dz} = -n(0)e^{-mgz/kT}\, mg = -n(z)mg\,. \tag{58}$$

Thus the pressure and density are consistent with the mechanics relation given in Eq. (56)